.STUDIES.ON.ELECTRIC..ENDOSMOSE.......

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by

...........ALVIN.STRICKLER...........

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To Professors:

.... *Mathews* ....

.... *Walton* ....

.... *Fischer* ....

....

This thesis having been approved in respect of
form and mechanical execution is referred to you for
judgment upon its substantial merit.

.... *Charles Dechter* ....
                                            Dean

STUDIES ON ELECTRIC ENDOSMOSE

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ALVIN STRICKLER   M S

A THESIS PRESENTED TO THE GRADUATE SCHOOL
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GENERAL INTRODUCTION

Whenever we have a membrane or its equivalent, that is, fine capillaries, or even a solid surface (or medium) in contact with a solvent (a liquid medium) there will be developed an electric double layer at the surface of contact. This will depend in magnitude and, in most cases, in nature, upon the relative dielectric constants of the solid and liquid media. If a difference of potential is now established in the liquid medium, either the liquid or solid will migrate, depending upon which is fixed, in the direction which depends upon the sign of the charge established by contact. This electric charge will be affected by the presence of any substance which may be adsorbed, as a molecule or ion, thus altering the nature of the surface. With the same potential gradient this will increase or decrease the flow according as such preferentially adsorbed substance bears a positive or negative charge or orients itself in such a way as to produce such charge. Adsorption of a neutral substance may also affect the flow by changing the dielectric constant ratio. Whether the adsorbed substance is neutral or charged depends upon the membrane, its nature and surface, the substance dissolved or suspended, and the liquid medium. Such phenomena are classed as electro kinetics.[1]

There are two types of electro kinetics:

Class A. 1. The membrane is fixed and the liquid medium free
to move. This is known as electric endosmose.

[1] Freundlich-Kapillarchemie.

2. The particles of solid migrate in the liquid
medium. This is known as cataphoresis.

Class B. 1. The above conditions may be reversed. If wat-
er is forced through fine capillaries a differ-
ence of potential will be established at the
ends of the capillaries. Such a phenomenis
illustrated by Quincke's diaphragm currents.[2]

2. The falling of small particles thru a liquid
may establish a difference of potential as
illustrated by the dropping electrode of Ost-
wald.[3]

This work has to do entirely with Class A[1]. Electric
endosmose is a necessary concomitant of all electrolysis in both
aqueous and non-aqueous solutions. It is affected by and affects
such electrolysis in a positive or negative manner depending upon
all factors which affect the nature of the membrane or solid med-
ium and the solution or liquid medium. Such solid medium may be
merely the container in which the experiment is carried out, though
a porous cup or membrane will make such effects much more apparent.

"The name endosmose is a misnomer"[4] because we have here
no difference in concentration of the two solutions separated by the

[2] Wied. Ann., 7, 351-1879.

[3] Zeit. Phys. Chemie., 1, 583 (1887).

[4] Bigelow, Theoretical & Physical Chemistry.

membrane, only as they become changed during the progress of the experiment. Such misnomers are quite frequent in chemical literature but the names are retained for traditional reasons. However; recent work by Bartell,[5] Bartell and Hocker,[6] and Jacques Loeb[7] shows that many of the peculiarities of "free osmosis" can only be explained by the theoretical consideration now applied to electric endosmose; and the relationship may not be so farfetched after all.

Practically all the experiments of a quantitative nature on this problem have been carried out with water as the liquid medium. Only in a few cases have other substances been used: liquid ammonia,[8] methyl alcohol,[9] and ethyl alcohol.[10] It was because of this and of the meager quantitative data in general that these researches were undertaken. Work was carried out with a number of typical non-aqueous solvents in an endeavor to determine if the principles and rules, applied to water, held for such. Besides certain preliminary work with water the following solvents were tested: acetone, amyl alcohol, nitrobenzene, pyridine, benzaldehyde and n-butyl alcohol. Using membranes of the same material and nature (filter paper) in each case the effects studied were: change of voltage, varying permeability of the

5 J. Am. Chem. Soc, 36, 646 (1914).

6 J. Am. Chem. Soc, 38, 1029 (1916)

7 J. Gen. Phys.," 1, 717 (1919); 2, 387; 563 (1920).

8 Ascoli-Comptes. rendus, 137, 1253 (1903).

9 Bandouin-Comptes. rendus, 138, 898, (1904).

10 Barrat & Harris-Biochem. Jou., 6, 315 (1912)
   Remy-Zeit. Phys. Chemie. 89, 467; 529 (1915)

membrane, presence of acid and alkali, addition of various cations
and anions, of varying concentration of the added salt, of the change
of temperature and of added water both to the pure solvent and to the
solvent containing a dissolved salt. From this data some very inter-
esting conclusions have been drawn.

HISTORICAL AND THEORETICAL INTRODUCTION

The phenomenon of electric endosmose was first observed
by Reuss in 1807,[11] working with two glass tubes (each containing
an electrode) which were filled with water, and placed upright in
a lump of clay. The clay acted as a membrane but not being very
firmly packed also tended to migrate in the opposite direction to
that of the water which rose in the cathode tube. So he secured
both phenomena of endosmose and cataphoresis.

Porrett[12] rediscovered the phenomenon in 1816 and it
was because he thought he detected an analogy with "free osmosis"
that the name in use was adopted. De la Rive,[13] Becquerel,[14]
Darriell,[15] and Napier[16] also studied the phenomenon in a similar
way but added nothing to its explanation.

[11] Memoires de la soc. imp. de naturalistas a Moseau,
2, 327 (1807).

[12] Thomsen's Jour. July, 1816.

[13] Traite' de l' Electr., 2, 379, (1825)
Ann. de Chim.et de Phys., 28, 125.

[14] Traite' de l' Electr., 3, 102 (1826).

[15] Ann. d. Physik u. Chemie, 1, 569 (1826).

[16] Phil. Mag. July, 1846.

In 1852-56 Wiedemann[17] took up the work and presented several generalizations. He used a porous clay cup containing a platinum electrode and placed this in a larger vessel of the solution to be studied containing the other electrode. A glass tube connected to the cup and passing horizontally over to a weighing bottle served to measure the amount of liquid passing into the cup. He also connected a manometer to this tube in his later experiments. But obviously a large error due to hydrostatic pressure must have been introduced in either case.

His conclusions were three:

1. The mass of liquid transported in unit time through a porous membrane is directly proportional to the strength of the electric current, and for a given membrane material and given current strength, it is independent of the length and sectional area of the membrane.

2. The difference in hydrostatic pressure maintained by electric endosmose between the two sides of a porous membrane varies directly as the current strength, and for a given membrane material and a given current, is proportional directly to the length and inversely proportional to the sectional area of the membrane; it is also proportional to the specific resistance of the liquid in the case of an aqueous solution.

3. For a given membrane material, the difference in hydrostatic pressure maintained between the two sides of a porous membrane is proportional to the applied potential and is independent

[17] Pogg. Ann., 87, 321 (1852); Wied. Ann., 99, 177 (1856)

of the dimensions of the membrane. So if H is the equilibrium
height, C the current, R the specific resistance, T the thickness
of the membrane and S the cross sectional area

$$H = constant \times \frac{CRT}{S}$$

Also since $\frac{RT}{S}$ represents the resistance of the membrane, the ex-
pression C $\frac{RT}{S}$ becomes CR' or it equals the potential fall between
the sides of the membrane, = E. So the formula becomes

$$H = constant \times E$$

He also concluded that the current caused the direct transport of
liquid (i.e. toward the cathode) by virtue of an attraction which
it exerted upon each element of volume of the liquid transferred.

This conclusion was contested by Graham,[18] V. Quintus Ici-
lius,[19] and Brede and Longemann[20] who showed that no transport of
liquid could be demonstrated unless a membrane or its equivalent
were present.

In 1853 Raoult[21] assumed the formation of compounds by
the products of electrolysis and the solvent; with a consequent
change of volume but submitted no experimental evidence to prove
his theory.

In 1856 Hittorf,[22] who was then carrying on some studies
on migration velocities of ions, said electric endosmose had no con-
nection with the velocity of the ions.

[18] Phil. Mag., 8, 151 (1854).

19 Lehrbuch der Experimental Physik, S. 642 (1855)

20 Ann. d. Physik u. Chemie., 100, 149 (1857)

21 Comptes rendus., 36, 826 (1853)

22 Pogg. Ann., 98, 9 (1858)

Weiske[23] in 1858 said, "There is an accumulation of elec-
tricity at the surface of contact of electrolytes and electrodes.
The less the conductance, the more important is this accumulation.
The cation is a better conductor than the anion; so when this good
conducting cation goes to the cathode it takes a negative charge
from that electrode which spreads over the cations, leaving no charge
on the cathode. In the case of anions they take a positive charge
at the surface of contact with the anode, but this charge does not
spread over the poor conducting anion and so the solution is driven
to the negative electrode. Though this theory is not clear, it is
important as a forerunner of the Quincke, Helmholtz theory which will
be cited later.

In 1860 Mattenci[24] considered electric endosmose as a phe-
nomenon entirely separate from electrolysis.

Wiedemann and Quincke in 1861[25] and Quincke in 1879[26]
studied the phenomenon in a capillary tube, considering a membrane
as merely a bundle of such tubes and advanced a theory which with
certain modifications is accepted today. It was during these re-
searches that Quincke forced liquid thru a porous membrane and found
that differences of potential were produced at opposite ends of the
membrane pores. These "diaphragm currents" gave rise to the law:

[23] Pogg. Ann., 103, 466 (1858)

[24] Comptes rendus, 51, 914 (1860)

[25] Pogg. Ann., 113, 513 (1861).

[26] Wied. Ann., 7, 351 (1879); Pogg. Ann., 107, 1(1859)
    -110, 38 (1860)

"When water is forced at a certain rate through a porous membrane the difference of potential produced is independent of the dimensions of the membrane but is proportional directly to the hydrostatic pressure."

Quincke considered electric endosmose as an electro capillary phenomenon depending upon the natural potential differences at the surface of separation of two unlike substances: solid and solution. In the case of clay and water the water in contact with the capillary wall is positively electrified and is therefore attracted to the cathode. He also said, the smaller the pore the greater the endosmose. If the solid is not fixed it will migrate to the electrode bearing a charge opposite to that established on it by contact. This flow will be continuous in most cases because there is a steady re-establishment of the double layer.

The experiments of these two men were very elaborate and important and they gave Helmholtz material for his mathematical theory of electric endosmose. They used distilled water and solutions of salts and acids and found that the addition of such electrolytes to pure water decreased the endosmose. Quincke found that the rate varied inversely as the fourth power of the diameter of the capillary tube used. Coated with shellac, the glass tube gave a greater flow but silver tubes gave less flow. He also noted that alcohol was slower than water and that turpentine in glass gave a reverse flow but if lined with sulphur the flow was toward the cathode again. Both state that the endosmose in equal periods of time is directly proportional to the intensity of the electric current and under like conditions independent of the area or thick-

ness of the porous wall.

Englemann[27] in 1874 tried the effect of different membranes with a rather unique apparatus and was one of the first to note that the presence of electrolytes changed the endosmose.

It was left to Helmholtz[28] to develop quantitatively and mathematically the qualitative results of Quincke. He put forth very clearly the idea of an electric double layer theory which had been previously suggested. The distribution of charges in this layer is such that the solid surface is charged oppositely to the liquid in contact with it and this orientation produces the electric double layer. He demonstrated by formulae that endosmose varied directly as the specific resistance of the solution, a contention which was later disproved by Holmes[29] in the case of certain nitrates.

Lamb[30] has shown that if the liquid is not a perfect insulator the application of a potential gradient will result in a continuous flow of liquid along the surface of the solid.

Freund[31] in 1879 found that with $Zn SO_4$ solutions endosmose varied inversely as the concentration.

Gernez[32] in 1879, from his studies, concluded that the addition to water or alcohol of any substance which changes the con-

[27]Arch. Neerland, 9, 332, (1874).

[28]Wied. Ann. 7, 337 (1879)

[29]Doctors Dissertation - Johns Hopkins University (1907).

[30]Phil. Mag., 25, 52 (1888).

[31]Wied. Ann., 7, 51 (1879).

[32]Comptes rendus., 89, 303 (1879).

ductivity would decrease the amount of liquid transferred.

Gore in 1880[33] speaks of negative endosmose with alcoholic solutions of barium bromide. With sixty-seven substances he found endosmose with all except KCN.

In 1890 Shaw[34], after a careful study of the problem, said that endosmose is a feature of the mechanism of electrolysis, the motion being due to a drift of complex ions made up of an ion of the salt attached to a large number of solvent molecules. Also Whetham[35] suggested that the inverse proportion of the concentration of the solution and electric endosmose shows that in dilute solutions the complex ion must carry many thousand molecules but it is not directly connected with electrolytic processes.

Coehn's work[36] gives a comprehensive expression to the double layer theory of Quincke and Helmholtz. As to why such an electric double layer should exist he suggests that, as the endosmose increases with the difference in dielectric constants of the membrane and solution, whenever two non-miscible substances, one of which is a pure liquid, are in contact, the substance with the higher dielectric constant is positive to that with the lower. Although he worked only with pure solvents, this rule has explained most subsequent phenomena under similar conditions. It must be remembered in applying this rule that the least trace of a charged adsorbable substance must naturally affect the charge, as will be seen in later work.

[33]Proc. Roy. Soc., 31, 253 (1880).

[34]B. A. Report, 202 (1890).

[35]Theory of Solutions., p. 292.

[36]Wied. Ann., 64, 227 (1898).

In the year 1903 Smoluchowski[37] developed the formula, which now bears his name, for the volume of liquid transferred in unit time through a single capillary.

After a series of masterly researches by Perrin in 1903-5[38] Freundlich in 1909[39] gave the present accepted expression to the formula for the volume of liquid transferred:

$$V = \frac{nr^2 \text{ e ED}}{4\pi\eta l} \quad [40]$$

where (n) is the number of capillaries under consideration, (r) the radius of the capillary, (e) the dielectric constant of the liquid, (η) the viscosity coefficient of the liquid and (l) the length of the capillary.

With a porous membrane, a bundle of capillaries, the equation becomes:

$$V = \frac{qe \text{ ED}}{4\pi\eta l}$$

where q is the cross sectional area of the membrane.

Since $E = RI$ and $R = \frac{1}{Vq}$ where V is the specific conductivity then:

$$V = \frac{eID}{4\pi\eta} = \text{constant} \times I$$

showing that the endosmose for a given liquid and membrane is proportional to the current strength, agreeing with Wiedemann's first

[37] Bull. d. I' Acad. d. Science de Cracovie. (1903).

[38] Jou. Chem. u. Phys., 2, 601 (1904)-3, 50 (1905). Comptes rendus., 136, 1388-137, 513 (1903).

[39] Kapillarchemie, 245 (1909); Zeit. Phys. Chem., 73, 385 (1906); Zeit. Phys. Chem., 79, 409 (1912).

[40] Taylor-Chem. of Colloids, p. 66.

law.[41] If, instead of allowing the liquid to escape, the pressure is allowed to rise

$$P = \frac{2e\ ED}{\pi\ r^2}$$

following Poiseuille's law for narrow capillaries.

In most instances, in the earlier work, the solution moved toward the cathode and the rule had been accepted that water in contact with any solid is positively charged. Perrin[42] found many apparent exceptions to this rule. He used an apparatus in which the membrane could be changed by disconnecting and refilling with a powdered substance. He measured the flow in a horizontal capillary tube but made no provision for the escape of gases produced during electrolysis. Using membranes of aluminium oxide, naphthalene, chromium chloride, silver chloride, barium sulfate, boric acid, sulphur, salol, carborundum, gelatine, and cellulose he studied the endosmose with water mainly but also tested it with other solvents. With chloroform, ether, petroleum, benzene and carbon disulfide he obtained no endosmose but secured a flow with methyl alcohol, ethyl alcohol, acetone, acetaldehyde and nitrobenzene. He tried the effect of acids and bases and of neutral salts of varying concentrations, the salts being dissolved in solutions already acidic or basic. He came to the following conclusion: "Every membrane tends to become positively charged against an acid solution and negatively charged against a basic solution. Every ion of unlike sign tends to neutralize this charge on the membrane and this tendency increases rapidly with the valence of the ion."

[41] Loc. Cit.

[42] Loc. cit.

Freundlich,[43] following, suggested a theory of "preferential adsorption" of ions to explain electric endosmose. If the cation is adsorbed most, the membrane becomes positively charged and if the anion is adsorbed most, the membrane is negative.

In 1900 Oleson[44] encountered the phenomenon of electric endosmose and in 1905 Hardy[45] observed that particles of gloubin in solutions of varying concentrations moved at the same rate.

In the years 1900 to 1904 and later some work was done which was bound to have a direct bearing upon theories pertaining to electric endosmose. In 1900 Nernst[46] showed how the problem of ionic hydration could be studied by means of diffusion and migration experiments, using an indifferent substance as an indicator. The same year Lotmar,[47] employing Nernst's method, found that hydration of ions actually occurs.

In 1904 Lobry de Bruyn,[48] using $Ag NO_3$ in aqueous methyl alcohol, found no evidence of hydrates or alcoholates but Morgan and Kanolt[49] when studying the electrolysis of

43   Loc. cit.

44   Am. Chem. Jour. 23.

45   Jour. of Physiol., 33, 351 (1905).

46   Nachr. d. K. Gesellsch. d. Wissensch. 1900.

47   Nachr. d. K. Gesellsch. d. Wissensch. 1900.

48   Jahrbuch d. Elektrochemie, 10, 260 (1904).

49   Zeit. Phys. Chemie, 48, 365 (1904).

$Cu(NO_3)_2$ in water and alcohol, concluded that copper ions were hydrated. Also Kohlrausch[50] thought it possible that ions in solution are surrounded by an atmosphere of solvent. Slow ions carry a large atmosphere and the rapid ions little. If this is true, then in electric endosmose, according to Holmes,[51] the slow cation would drag along a larger amount of liquid than the more rapid less solvated ions.

In 1903 Ascoli[52] applied Perrin's rule to liquid ammonia and in 1904 Bandouin[53] to methyl and ethyl alcohol solutions. They found no exceptions.

In 1903 Bancroft[54] issued a short note on electric endosmose but added nothing to the explanation of the phenomenon.

In 1904 Billitzer[55] proposed a theory of capillary phenomena which doubtless had considerable effect upon later theories of electric endosmose.

In 1906 Morse, Frazer and Hopkins,[56] studying osmotic pressures of solutions of glucose, used electric endos-

50. Proc. Roy. Soc., 71, 348.

51. Loc. Cit.

52. Comptes rendus., 137, 1253 (1903).

53. Comptes rendus., 138, 898 (1904).

54. Trans. Am. Elec. Soc., 3, 261 (1903).

55. Zeit. Phys. Chemie., 48, 513 (1904).

56. Am. Chem. Jour., 36, 40 (1906).

mose for removing air from their membranes. To increase the
rate they dissolved various salts in the water and concluded
that the quantity of water carried through porous walls under
identical conditions is inversely proportional to the velocity
of the cation divided by the valence.

Holmes in 1907[57] and Fraser in 1908[58] developed
elaborate types of apparatus for the study of electric endosmose.
One was an overflow type in which the amount of liquid was
weighed, the other a type in which the movement of a bubble
in a capillary tube measured the rate of flow. The membranes
used were porous clay cups. They found, contrary to Helmholtz's
statement,[59] that the endosmose of solutions of nitrates through
a clay membrane was not directly proportional to the relative
specific resistance, but that it does vary with the velocity
of the cation divided by the valence. They also suggested that,
following the views of Kohlrausch[60] and others on the hydration
of ions, using the same anion, the endosmose should vary in-
versely as the velocity of the cation. So the extent of hy-
dration must be an important factor in electric endosmose.

57   Doctor's Dissertation, Johns Hopkins University.

58   Am. Chem. Jour., 40, 319 (1908).

59   Loc. cit.

60   Loc. cit.

Haber and Klemensiewicz in 1909[61] suggested, for the case of glass against water, that the solid is essentially a hydrogen electrode and the magnitude of the potential difference depends upon the concentration of hydrogen ions in solution. But Freundlich[62] has shown that hydrolysis of the solute does not determine electric endosmose and that, while acidity and alkalinity have a great influence, they are not the only determining factors.

Coehn,[63] continuing his work in 1910, found that H_2SO_4 always went to the cathode but that HNO_3 showed an isoelectric point of reversal, as did acetic acid, at a definite concentration. Neutral sulphates and alkali nitrates flowed to the cathode while heavy metal nitrates flowed to the anode unless extremely dilute.

In 1912 several contributions were made to the study of this phenomenon. Bancroft[64] suggested a theory of preferential adsorption of ions, following Freundlich, and said: "The sign of the charge on a membrane depends upon the relative adsorption of cation and anion; being positive if the cation is adsorbed to a greater extent and negative if the reverse is the case." With such a postulation he readily explained most phenomena which had puzzled other investigators. He also added

61. Zeit. Phys. Chem., 67, 413 (1909).

62. Loc. cit.

63. Zeit. Elektrochemie, 16, 589 (1910).

64. Jour. Phys. Chem., 16, 312 (1912).

that we can no longer maintain that the potential difference
between a metal and an aqueous solution is a function of the
concentration of the metal alone. It will vary with the nature
of the anion and other cations present in so far as they are
adsorbed by the metal in question.

In the same year Barrett and Harris[65] carried on some
extended research in an endeavor to introduce dissolved sub-
stances into living tissue by electric endosmose. Their ap-
paratus was very similar to that used by Perrin[66] and they
studied gelatine, agar and parchment paper as preliminary to
their tissue experiments. They used varying concentrations and
confirmed in the main the valence rule of Perrin, for both
water and alcohol solutions. They concluded that the flow of
liquid is obviously determined by the movement of ions in the
liquid at the surface of content. These ions cause a passive
movement of the liquid in the same direction as the current.
Such ions may also be hydrated thus carrying the liquid along
with them but they asserted that this plays probably only a
subordinate part. They found that non electrolytes had no ef-
fect upon the direction or amount of endosmose. Working with
salt solutions of different concentrations they noted that the
end osmose reached a maximum at a definite concentration de-
pending upon the nature of the membrane.

65   Biochem. Jour., 6, 315 (1912); Zeitschr.Elektrochem.,
     18, 221 (1912).

66   Loc. cit.

In 1912 also, Elissafoff[67] used Lemstrom's method[68] of a capillary tube filled with water or electrolyte and supported between two discharge points in a horizontal position, the discharge furnishing the potential gradient. He made an elaborate study of neutral solutions and found that Perrin's rule held only to a limited extent. With the alkali metals and the alkaline earths it was satisfactory but not with the heavy metals or organic cations. He also noted that the cations were more effective than the anions but that ions and cations of heavy metals and basic dyes have a much greater effect than corresponds with the valency. There is a clear parallelism between the effect of electrolyte on endosmose and the precipitation of suspension colloids and both phenomena can be explained by selective adsorption.

In 1913 Freundlich and Elissafoff[69] determined the valence of radium by means of electric endosmose, emplpying the valence rule of Perrin.

In 1912 Bartell[70] while working on pore diameters was led, *by his conclusions* to carry out in 1914[71] some work on negative "free osmosis" which was continued with Hooker in 1916.[72] He con-

67. Zeit. Phys. Chemie., 79, 385 (1912).

68. Drudes Ann., 5, 729 (1901).

69. Phys. Zeit. 14, 1052 (1913).

70. Jour. Phys. Chem., 16, 318 (1912).

71. J. Am. Chem. Soc., 36, 646 (1914).

72. J. Am. Chem. Soc., 38, 1039; 1036 (1916).

cluded that negative "free osmosis" is closely related to electric endosmose. The flow of liquid through a membrane in such cases is brought about by a difference in potential at the two ends of the capillaries of the membrane, which have become in some way oppositely charged. The sign of this charge depends upon the relative adsorption of the anion and cation. He also added that the magnitude of the charge is dependent upon a difference in migration velocities of the ions in the membrane pores.

In 1914 Doumer[73] observed some curious hydration and de-hydration effects during electric endosmose with gelatine.

Byers and Walter this same year[74] made some interesting qualitative experiments with cells of an overflow type containing several membranes. They concluded that endosmose will cause flow with the current, against the current or in both directions at the same time. Forgetting, however, that they were working with more than one membrane they failed to see how an adsorption theory could account for the transversal of the plates by water.

In 1914 also Bethe and Toropoff,[75] although their data is incomplete, suggested that the Hoffmeister series plays an important part in electric endosmotic effects. They dis-

73. Comptes rendus., 76, 40, (1914).

74. J. Am. Chem. Soc., 36, 2284 (1914).

75. Zeit.Phys.Chemie., 88, 648 (1914); Zeit.Phys. Chemie., 89, 637 (1915).

cussed a number of experiments with gelatine, albumen, collodion, animal and other membranes and concluded that the interface potential is an ionic adsorption phenomenon and that the flow depended upon this and the relative hydration of mobile ions. Their apparatus did not provide for any escape of gases produced by electrolysis.

In 1915 Remy[76] employed endosmotic methods for determining the degree of hydration of ions. His apparatus was rather unique but again provided for no escape of gases. He calculated the transport of solution per Faraday. To do so it was necessary to subtract the specific endosmose of the pure solvent, thus obtaining the amount of water carried by the ions. Helmholtz[77] had earlier developed a formulae for the specific endosmose of a pure solvent:

$$Os = C \ \frac{M.L}{Et}$$

where (M) is the actual flow, (L) the length of electrolyte, (E) the potential drop over L, (t) the time and (C) a constant depending upon the capillary. This formula becomes

$$Os = C \ \frac{M}{Q} \cdot \frac{1}{W}$$

if (Q) is the quantity in coulombs and (W) the resistance in ohms. But $\frac{1}{W} = X =$ the conductivity, hence

76. Zeit. Phys. Chemie., 89, 467; 529 (1915).

77. Loc. cit.

$$Os = C \quad . \quad \frac{MX}{Q}$$

factors which could easily be measured. From his measurements, which were very extensive, he concluded that, besides endosmose, a transport of water takes place due to hydration and further that Perrin's results were merely qualitative because they did not admit of a quantitative estimation of such influence.

Bancroft in 1915 and 1916[78] carried out some work on colloids and suggested that any surface is able to adsorb substances from a liquid with which it is in contact. Such surface may adsorb a particular ion selectively thus producing a positive or negative charge on the solid. The adsorbing substance tends to be peptized by the adsorbed ion. Solids may adsorb the solvent itself and be peptized or they may adsorb a non electrolyte, an undissociated salt or another solid in collodial suspension.

These conclusions furnished the material for Brigg's[79] theory of electric endosmose as presented in 1917. He has made in his writings a masterly summary of all the work leading up to the development of electric endosmose at that time. With his coworkers he developed a form of apparatus quite unique in its method for measurement and ease of operation. It consisted of two chambers separated by a porous membrane and connecting through a horizontal tube containing a bubble of air, the movement of which recorded the rate of endosmotic flow. It also provided

78. Jour. Phys. Chem., 19, 351 (1915); Jour. Phys. Chem. 20, 85 (1916).

79. Jour. Phys. Chem., 21, 198 (1917); Jour. Phys. Chem., 22, 256 (1918); Report of the British Assoc. for Adv. of Science (1918).

for the escape of gases produced by electrolysis. He used
water solutions and found that the rate of endosmose is propor-
tional to the applied potential under unchanged conditions. Also
that the rate increases with rising temperature, not exactly
proportional to the fluidity, but slightly less rapidly to
conform to the equation:

$$V = \text{constant} \times \frac{ED}{\eta}$$

for a given diaphragm and liquid. He confirmed Perrin's data[80]
and studied the electric endosmose with copper salts and the
relation to dyeing of contact electrification. From a study of
his own and previous data he formulated a general theory:

    1. "Electric endosmose depends upon the preferential
or selective adsorption of ions and is influenced only by
those ions which are adsorbed by the membrane."

    2. "Any circumstance or condition which changes the
adsorption produces an effect. It varies therefore with the
condition of the surface, the relative and absolute ion concen-
tration, temperature and so forth."

    3. "The direction indicates the sign of the membrane;
the rate is proportional to the intensity of the charge in case
the potential gradient through the membrane is constant. If
liquid flows to the cathode the membrane is negative, when to
the anode the membrane is positive. No flow indicates an iso-
electric condition."

    80. Loc. cit.

4. "A membrane tends to become positive by selective adsorption of cations and negative by selective adsorption of anions".

5. "The positive charge produced by an adsorbed cation is neutralized more or less by the addition of an adsorbed anion. Similarly the reverse is true."

6. "Electric endosmose measures the tendency of a solid to form an electrical suspension in a given liquid but it does not measure the tendency of a solid to form a non-electrical suspension; such as is produced by adsorbed solvent, solute, or neutral colloid."

In 1919 Weiser and Sherrick[81] carried out some experiments on the order of adsorption of ions by Ba SO_4. They found that changing conditions affect the order but not the amount. Also that there are two factors determining the adsorption of a given adsorbing agent; the nature of the ion and its valence. With similar ions the specificity of adsorption is not so pronounced as the valency factor. This might also apply in the case of other adsorption phenomena.

The most recent published work pertaining to electric endosmose is that by Loeb, 1919 and 1920.[82] This work was carried out to determine the influence of electrolytes on the electrification and rate of flow of water through collodion membranes and the cause of this influence. His apparatus was very crude, being merely a collodion sack with a capillary tube containing an electrode attached. This was

81. Jour. Phys. Chem., 23, 205 (1919).

82. Jour.Gen.Physiology. 1,717(1919); Jour.Gen.Phys.,2, 387; 563 (1919).

placed in a beaker of solution containing the other electrode. Measurements were taken in the capillary tube. This, of course, did not admit of the escape of gases.

He showed that in electric endosmose through collodion membranes the influence of an electrolyte on the rate of transport is the same as in "free osmosis." Both positive and negative "free osmosis" must be explained as an electric endosmotic phenomenon due to the production of a double layer and its consequent change under the influence of adsorbed ions. As the concentration curves show a maximum, he concluded that the density of the electric double layer increases with an increase in concentration at lower concentrations, while at higher concentrations it decreases with a corresponding increase in concentration of the electrolyte.

This work and that of a more recent date[83] on the reversal of the sign of the charge on a membrane by hydrogen ions has added materially to our explanation of phenomena which depend upon contact electrification and adsorption.

Girard and Morax[84] carried out a series of interesting endosmotic experiments on the eye of a rabbit. The cornea acted as the membrane which was bathed on the inside by the aqueous humor and on the outside by an electrolyte solution. Their conclusions were strictly biological.

83. Jour. Gen. Physiology, 2, 577 (1920).
84. Comptes rendus, 170, 821 (1920).

"The commercial applications of electrical osmosis"
was the title of a paper by Highfield, Ormandy and Laurie[85]
in which they gave a comprehensive review of the commercial
possibilities of endosmose in the ceramic industry.

Frank and Withrow[86] encountered the phenomenon in
some work on alkali solid amalgams but added nothing new to
the problem.

It will be seen that practically all this work has
been done on aqueous solutions, or partly aqueous; and it was
because of this that these researches were undertaken to note
the same effects in some typical non aqueous solvents. Further-
more, the only apparatus which provided for an escape of the
gases formed was that of Briggs[87] and though this would not
be a highly disturbing factor with such solvents, the same
precautions were taken.

APPARATUS

The apparatus used in these experiments was, as
illustrated, a modification of the Briggs[88] type. It con-
sisted of two chambers M and N alike in construction except
that the right-hand one contained a three way stop cock, C,
for the purpose of getting the air bubble in the tube D.
Tube D, the measuring or bubble tube, was a 2.5 m.m. tube,
16 inches long on the horizontal, bent as shown with vertical

85. Pottery Gaz. 45, 775 (1920).

86. J. Am. Chem. Soc., 42, 671 (1920).

87. Loc. cit.

88. Loc. cit.
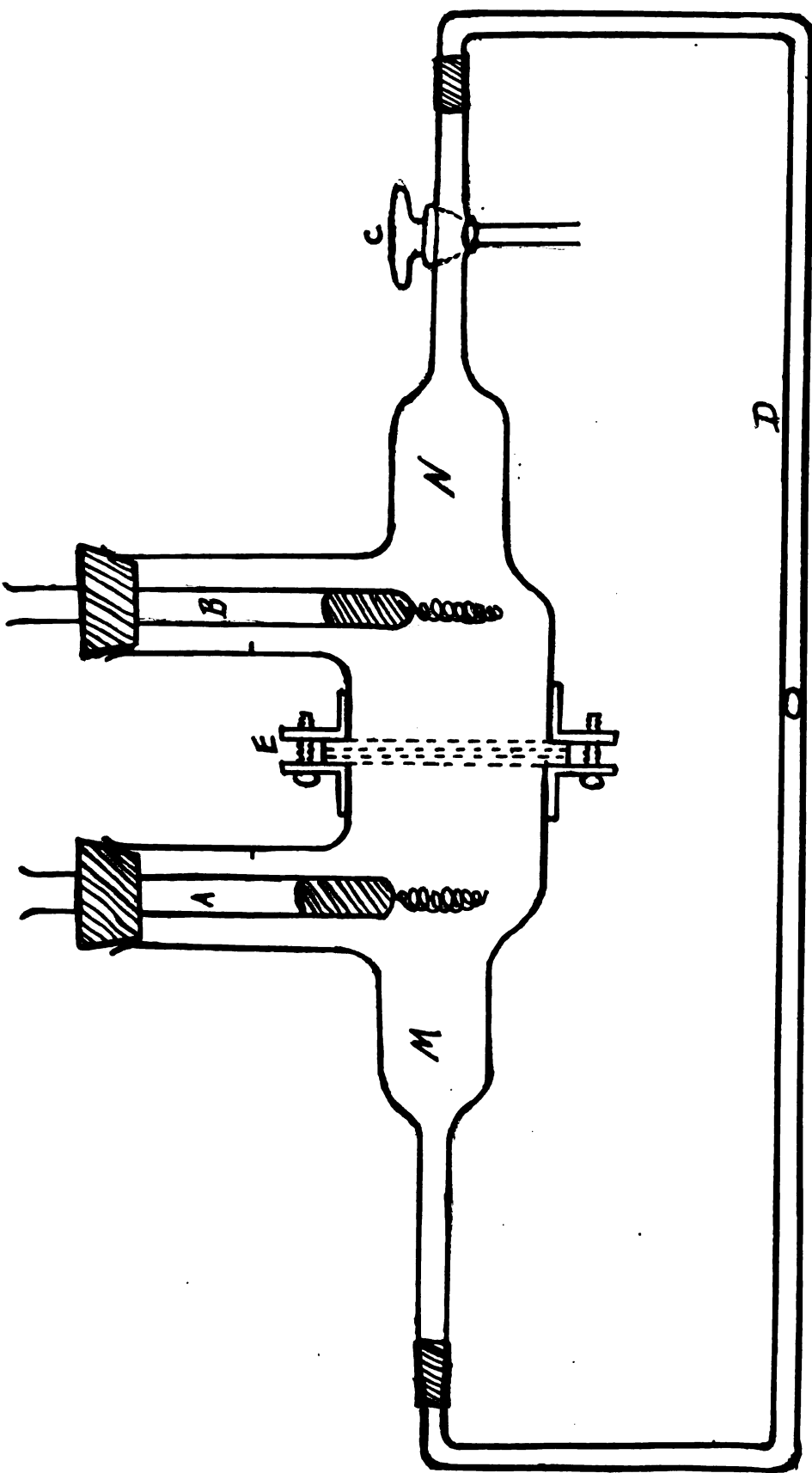
sections 4 inches long. It fitted snugly against the ends of the chamber outlets, connected there by short pieces of rubber tubing. When making the run this was placed in front of a permanent millimeter scale immersed in the constant temperature bath.

The two electrode chambers M and N were reduced in size and volume by constricting the original $1\frac{1}{4}$ inch tubing down to a diameter of 3/4 of an inch. The vertical tubes were 5/8 of an inch in diameter, to give ease in filling and cleaning. As this would tend to decrease the sensitivity, large tubes A and B containing the electrodes, with mercury contact, were used. Under such conditions a small increase in the volume of liquid, the surface of which was already up in this tube, created sufficient pressure to force the solution around through the bubble tube D. Further, the use of a single stop cock (C), unlike Briggs' apparatus, filled the measuring tube with the same solution as that in the chamber; a condition absolutely necessary when using non-aqueous solutions. The upright tubes were sealed in on the shoulder of the original chamber to prevent the collection of bubbles which might affect the volume.

As an additional feature, the apparatus was made in two units, connected at E, with brass rings bearing a flange and screws for bringing them tightly together. These were sealed to the glass with litharge glycerine cement and at the edge filled in with a water insoluble cement. Although the ends of the glass chambers had been carefully ground and the

rings accurately machined, these joints were now ground down
with very fine emery cloth until they fitted almost perfectly
together. This arrangement made the apparatus very easy to
clean and greatly increased its usefulness for such membranes
as filter paper. When powdered substances were used the mem-
brane was built up in a glass ring, as explained later, and
then set in rubber gaskets and screwed tightly into place.
This gave a very sensitive measuring instrument usable under
greatly varying conditions. The stoppers carrying the elec-
trodes were grooved to allow for the escape of any gases pro-
duced by electrolysis.

To secure constant temperatures, an oblong bath
26 x 6 x 8 inches was constructed of heavy galvanized iron.
This contained a window in one side (20 x 4 inches) and the
whole was suspended on a frame made of 3/8 inch piping so that
the window came at just the level of the eye. In the bottom at

one end was an inlet tube 1/2 inch in diameter, which just
passed through the tank, and at the other end an outlet tube
1 inch in diameter and extending to within 1 inch from the top.
Across the top of this tank was placed a horizontal rod bent at
right angles at each end and raised about 4 inches. This was
securely fastened to the heavy steel edge of the tank and served
as a suspension for the apparatus. The apparatus itself was
set firmly in two clamps, one at each end on the constricted
part of the chamber, which were then fastened to a steel bar.
This could be lifted from its position outside the bath, after

filling, and set into the bath where this steel bar was secured by other clamps fastened to the horizontal bar. This made it possible to always have the apparatus in exactly the same position and further aided in the ease of manipulation. Water was pumped into this tank from a covered thermostat, kept at a constant temperature and overflowed directly back into the thermostat again. Tests showed that the temperature did not vary more than $\pm 0.01^{\circ}$ throughout the tank in which the readings were taken.

For the determination of the permeability of the membrane, the apparatus with electrodes and bubble tube removed was clamped in a vertical position, with the stop cock at the bottom. By means of rubber tubing, the top of the apparatus was connected to a dropping funnel, of large capacity, containing the solution. Attached to the how horizontal opening of the stop cock was a tube of the same size as the bubble tube (2.5 m.m.) placed in an exactly level position beside a meter stick. The solution was now allowed to run from the dropping funnel into the upper chamber until it overflowed through the electrode tube into a waste bottle. This overflow was maintained, thus keeping a constant head above the membrane. When this constant head was reached the solution was directed into the horizontal capillary tube by turning the stop cock and the rate per second recorded. The results were found to check very well.

SOURCE OF VOLTAGE

The first runs were made by using the storage battery system as a source of voltage but the maximum obtainable from this source was only 130 volts and it was found to fluctuate a great deal due to other demands upon it. As no current, or very little, was needed in the case of non aqueous solvents it was decided to set up a series of flash light batteries which, if no current was drawn, would give a constant voltage for a long period of time. Six hundred and ninety of these batteries,[89] such as are used for radio work, were obtained. To the side of each (negative pole) was soldered a piece of copper wire 2 inches long. They were then placed upright in three trays, in rows of ten each, after first pouring in a thin layer of a mixture of paraffine and beeswax in the bottom and slightly warming the battery before setting it in. A mixture of paraffine and beeswax was then poured into the trays until the batteries were about 3/4 immersed. This was allowed to harden and thus formed an insulator between them about one-half inch thick. The copper wire which had been soldered to the negative pole was then bent over and soldered to the center positive pole of the next battery until the whole system was in series. Wires were soldered on so that the voltage could be taken off the binding posts at the edge of the trays in sets of forty batteries each. The accompanying chart, Table I, shows how much voltage was obtainable and how well the system held up during the series of experiments. Besides the dates indicated, checks were made after each set of runs to see if sufficient change had occurred to make a new table necessary.

89. Burgess Co., Madison, Wis.

TABLE 1

BATTERY VOLTAGES

Connection Binding Post	D A T E				
	March 31	April 14	May 7	May 27	June 21 July 8
1 to 2	58.5	58.0	56.0	55.0	54.0
1 - 3	116.0	115.0	111.0	109.0	107.0
1 - 4	175.0	173.0	167.0	164.0	162.0
1 - 5	232.5	231.0	223.0	218.0	216.0
1 - 6	290.5	289.0	279.0	273.0	271.0
1 - 7	348.5	347.0	336.0	329.0	326.0
1 - 8	406.5	404.0	393.0	384.0	381.0
1 - 9	465.5	461.0	451.0	441.0	437.0
1 - 10	524.5	519.0	508.0	498.0	493.0
1 - 11	583.5	576.0	566.0	555.0	549.0
1 - 12	648.5	633.0	623.0	612.0	605.0
1 - 13	701.5	690.0	679.0	669.0	659.0
1 - 14	760.5	748.0	736.0	727.0	716.0
1 - 15	819.5	806.0	793.0	785.0	772.0
1 - 16	878.5	863.0	849.0	841.0	827.0
1 - 17	937.5	921.0	906.0	898.0	883.0
1 - 18	996.5	979.0	963.0	955.0	939.0
1 - 19	1011.5	994.0	978.0	971.0	954.0

In setting up such a system it is advisable to have
the two connections as far apart as possible when drawing high
voltage. This precaution prevents short circuiting due to a
moisture layer on the wax. To attain this the batteries were
placed in short rows rather than long ones and the lead wires
connected as indicated.
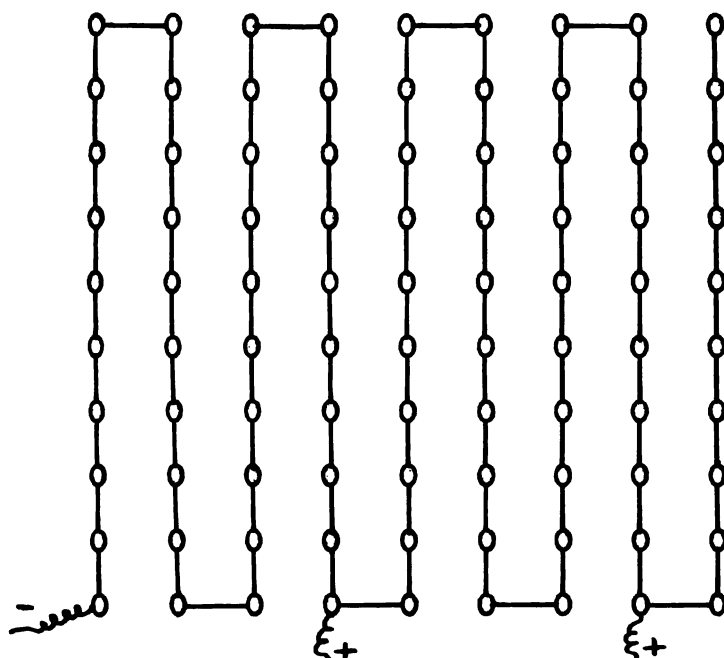
It must also be remembered that such a system is only
practical when a very low current, or none, is desired. This
was quite manifest when the batteries showed a rapid decrease
during certain water runs where comparatively high amperage
was used. The current was transported to the apparatus through
ordinary light cord which dipped into the electrodes with mercury
contacts. In the circuit was also a fuse plug to protect the
milliameter and a reverser to change the direction of the current
through the apparatus. A voltmeter was connected across the
electrodes. As the volt meter only read to 150 volts, and no

larger direct current instrument was obtainable, it was dis-
connected except when checking up the batteries. These were
read in sections of forty each and the total secured by adding
the readings.

EXPERIMENTAL PART

The apparatus, as described, had a volume of about
80c.c. It was found necessary to keep the parts, particularly
the bubble tube, scrupulously clean to prevent bubbles of gas
from sticking and the measuring bubble from adhering to the
tube. This was accomplished by filling with ohromic acid
cleaning solution at the end of each day's runs. This also
made it necessary to rinse thoroughly to rid the walls of any
acid which, having been absorbed by the membrane, might affect
its charge. On a few occasions the apparatus had to be taken
down and rinsed again to remove such impurities. The presence
of grease could be easily detected by a distortion and sticking
of the bubble. After washing, the apparatus was dried by drain-
ing and a stream of air and then rinsed with the solution to
be used in the run.

One section of the apparatus was now clamped in a
vertical position with the brass connection upward. Upon this

was placed the membrane. If the glass section in which the membranes were first built up was to be used, rubber gaskets were employed to give a tight joint. If filter paper was used, as in most of the experiments, the membrane was merely laid on the connecter and the other section secured firmly in   place. This gave a non-leakable joint without gaskets. The filter papers used had been soaked for at least twelve hours in the solution to be measured and then pressed firmly to eliminate any small air bubbles.

The apparatus, containing its membrane, was now clamped in a horizontal position, as previously indicated, and the bubble tube connected on by means of short pieces of rubber tubing. It will be noted that the stop cock is on the right-hand section. Solution was poured into this section, with the stop cock closed, until the electrode tube was about one-half full. The stop cock was then opened just enough to fill the opening in it with liquid and then closed. The left-hand chamber was filled to about the same height and care takento remove all air bubbles. This left the bubble tube still empty. It was filled by first opening the stop cock so that the flow was directed into a beaker and then by blowing lightly into the left electrode tube through a large piece of tubing which just fitted into the top. This forced the solution around through the bubble tube until it was entirely filled except for a small air bubble. Turning the stop cock so that it opened into the chamber, the air bubble was forced back into the horizontal part of the measuring tube, by blowing on the right electrode

tube, and the cock was closed. After a little experience it was found to be a very simple matter to get a bubble of the desired size very quickly. It should also be noted that, unlike Briggs' apparatus, which had distilled water in the bubble tube, this one had the solution throughout the entire system. This condition was absolutely necessary with non aqueous solvents and seems advisable in any case to prevent changes in concentration of the solution in the chambers. The apparatus was then filled to the marks on the electrode tubes. Before the electrodes were inserted and the stop cock opened the solution was forced back and forth through the membrane at least fifteen times by blowing on the electrode tubes as stated in filling. This process by flushing out the pores of the membrane gave it a chance to adsorb such ions as were present in solution and established a uniformity of conditions otherwise difficult to obtain.

Great care was taken to see that the stop cock was opened wide. This was found to cause considerable error in several experiments so that the maximum opening was marked and the stop cock always placed in this position.

The apparatus was now lifted and clamped into position in the bath where it was allowed to come to equilibrium. The bubble tube was leveled by a permanent level wire stretched horizontally across the window. The contact wires placed in the electrode mercury cups made it ready for reading.

The current was sent through the apparatus and the bubble timed with a stop watch for a movement to the right or

left. If very rapid, the flow was allowed to continue nearly
the whole length of the tube (30 cm.). The current was then
reversed and the reverse flow timed. This was continued for
10 to 30 passages and the average taken as the rate of endos-
motic flow. No movement was ever detected unless the current
was on, showing the absence of leaks. This was further tested
by allowing the filled apparatus to stand over night with no
apparent change in volume.

     Before taking the apparatus apart to renew the mem-
brane and solution, it was emptied and the rate of permeability,
for the particular membrane employed, determined in the manner
previously described. The entire operation required in most
cases less than one-half hour. The Tables 2 to 8 and their
accompanying curves illustrate the changes in rate during a
long continuous run and why it was necessary and desirable in
most cases to take an average of the first few readings only.

TABLE 2

January 13, '20.

Voltage - 17.0   Current 2.0   Temp. 25°   Bubble 6 m.m.
Solution H_2O Membrane (6 gm. Asbestos Vacuum 15 in)
Osmose + (No. of sec. for 30 cm.)

L	1	2	3	4	5	R	1	2	3	4	5
	133.2	129.8	128.0	126.2	125.0		129.8	123.2	124.2	122.6	121.5
	6	7	8	9	10		6	7	8	9	10
	124.0	122.0	120.8	120.5	120.2		120.4	118.4	117.8	116.4	117.2
	11	12	13	14	15		11	12	13	14	15
	119.4	____	118.8	118.6	117.4		117.0	115.6	116.5	116.2	115.0
	16	17	18	19	20		16	17	18	19	20
	116.5	118.8	117.8	117.4	117.0		115.8	115.0	115.2	115.5	116.6
	21	22	23	24	25		21	22	23	24	25
	117.0	117.0	116.0	116.8	116.8		115.6	116.8	115.8	115.4	114.8
	26	27	28	29	30		26	27	28	29	30
	116.2	116.8	116.4	117.8	117.6		____	116.2	115.5	116.6	116.2
	31	32	33	34	35		31	32	33	34	35
	118.0	117.4	117.5	____	118.6		117.5	116.4	116.8	117.2	117.0
	36	37	38	39	40		36	37	38	39	40
	119.0	117.0	118.0	118.4	120.0		117.8	117.2	117.2	117.8	120.2
	41	42	43	44	45		41	42	43	44	45
	120.2	118.8	115.0	117.8	116.0		119.4	120.8	115.8	119.0	115.0
	46	47	48	49	50		46	47	48	49	50
	117.0	116.4	120.6	121.2	121.4		120.0	116.8	116.0	120.0	121.2

TABLE 3

April 6. '20.

Voltage 406.5   Current 0   Temp. 25°   Bubble 6 m.m.
Solution - Acetone   Membrane (8 Thickness S.& S.
Osmose + (Sec. for 30 om.)   Paper No.589)

L	1	2	3	4	5	R	1	2	3	4	5
	24.5	22.8	21.8	21.4	21.5		26.4	22.8	21.6	21.8	22.0
	6	7	8	9	10		6	7	8	9	10
	21.4	21.0	20.8	21.8	21.8		20.8	21.5	21.4	21.0	22.4
	11	12	13	14	15		11	12	13	14	15
	22.0	22.6	22.8	23.0	23.0		21.4	22.4	22.6	22.6	23.0
	16	17	18	19	20		16	17	18	19	20
	23.5	24.0	24.4	24.2	24.8		23.0	23.6	23.5	23.5	23.5
	21	22	23	24	25		21	22	23	24	25
	24.5	24.8	25.0	25.5	25.2		24.0	24.0	24.2	24.0	25.0
	26	27	28	29	30		26	27	28	29	30
	27.0	27.0	27.0	27.2	26.5		24.9	27.5	26.5	26.5	25.8
	31	32	33	34	35		31	32	33	34	35
	27.5	27.4	27.8	28.8	28.0		26.0	26.8	27.8	____	27.8
	36	37	38	39	40		36	37	38	39	40
	28.0	28.8	29.8	29.2	28.2		28.0	28.4	28.8	29.5	29.0
	41	42	43	44	45		41	42	43	44	45
	30.0	30.8	30.0	30.5	31.6		29.5	29.8	30.5	30.0	30.0

TABLE 4

May 13, '20

Voltage 623.0   Current 0   Temp. 25°   Bubble 4 m. m.
Solution - Amyl alcohol   Membrane (6 thickness S S No. 589)
Osmose - (Sec. for 15 cm.)

L	1	2	3	4	5	R	1	2	3	4	5
	96.8	99.0	95.0	92.5	91.6		97.0	98.2	97.0	94.0	93.0
	6	7	8	9	10		6	7	8	9	10
	93.0	92.4	94.0	94.8	95.0		94.8	94.0	93.0	94.8	96.0
	11	12	13	14	15		11	12	13	14	15
	97.0	97.0	98.2	98.0	98.8		97.0	97.0	97.0	97.5	99.0
	16	17	18	19	20		16	17	18	19	20
	99.4	98.8	97.4	100.4	100.8		98.5	98.5	98.5	101.5	102.8
	21	22	23	24	25		21	22	23	24	25
	101.5	102.0	103.0	105.5	106.0		102.0	104.0	105.5	103.8	107.5

TABLE 5

May 31, '20.

Voltage 555.0   Current 0   Temp. 25°   Bubble 3.0 m.m.
Solution - Nitrobenzene   Membrane (8 thickness S & S 589)
Osmose + (Sec. for 15 cm.)

L	1	2	3	4	5	R	1	2	3	4	5
	18.0	17.0	16.8	17.4	17.4		18.0	17.2	17.5	17.8	18.2
	6	7	8	9	10		6	7	8	9	10
	17.8	18.4	20.0	20.0	21.0		19.0	19.6	19.6	21.0	22.0
	11	12	13	14	15		11	12	13	14	15
	23.0	26.8	28.0	34.0	37.0		25.2	26.0	31.0	32.5	35.5
	16	17	18	19	20		16	17	18	19	20
	41.8	48.8	49.0	50.8	49.0		40.5	41.2	42.5	44.0	46.4

TABLE 6

June 12, '20.

Voltage 841.0   Current 0   Temp. 26.5^{0} Bubble 5.5 m.
Solution - Pyridine   Membrane (6 thickness S & S No.589)
Osmose +(sec. for 10 cm.)

L	1	2	3	4	5	R	1	2	3	4	5
	117.0	122.5	120.5	127.5	123.0		118.0	119.0	118.0	119.5	117.0
	6	**7**	**8**	**9**	**10**		**6**	**7**	**8**	**9**	**10**
	124.0	124.0	123.0	123.8	126.0		119.0	119.5	119.0	121.0	128.6
	11	**12**	**13**	**14**	**15**		**11**	**12**	**13**	**14**	**15**
	125.0	124.0	126.5	124.4	125.0		120.5	120.5	124.0	122.5	124.0
	16	**17**	**18**	**19**	**20**		**16**	**17**	**18**	**19**	**20**
	127.0	131.5	131.0				126.8	131.0	129.0		

TABLE 7

June 21, '20.

Voltage 954.0   Current 0.5   Temp. 25^{0} Bubble 4.5 m.m.
Solution - benzaldehyde   Membrane (8 thickness S & S No.589)
Osmose + (sec. for 10 cm.)

L	1	2	3	4	5	R	1	2	3	4	5
	45.0	41.0	47.0	57.5	57.0		52.0	48.0	56.5	55.0	58.0
	6	**7**	**8**	**9**	**10**		**6**	**7**	**8**	**9**	**10**
	58.0	59.0	59.8	60.0	61.2		62.0	66.0	70.8	75.0	81.0
	11	**12**	**13**	**14**	**15**		**11**	**12**	**13**	**14**	**15**
	64.0	65.8	68.5	69.5			93.0	109.0	137.0		

For Table 2.

Right   Sec. for 30 cm.   Left

For Table 3.

No. of rur.

For Table 4.

For Table 5.

No. of run.

For Table 6.

For Table 7.

No. of run.

For Table 8.

No. of run.
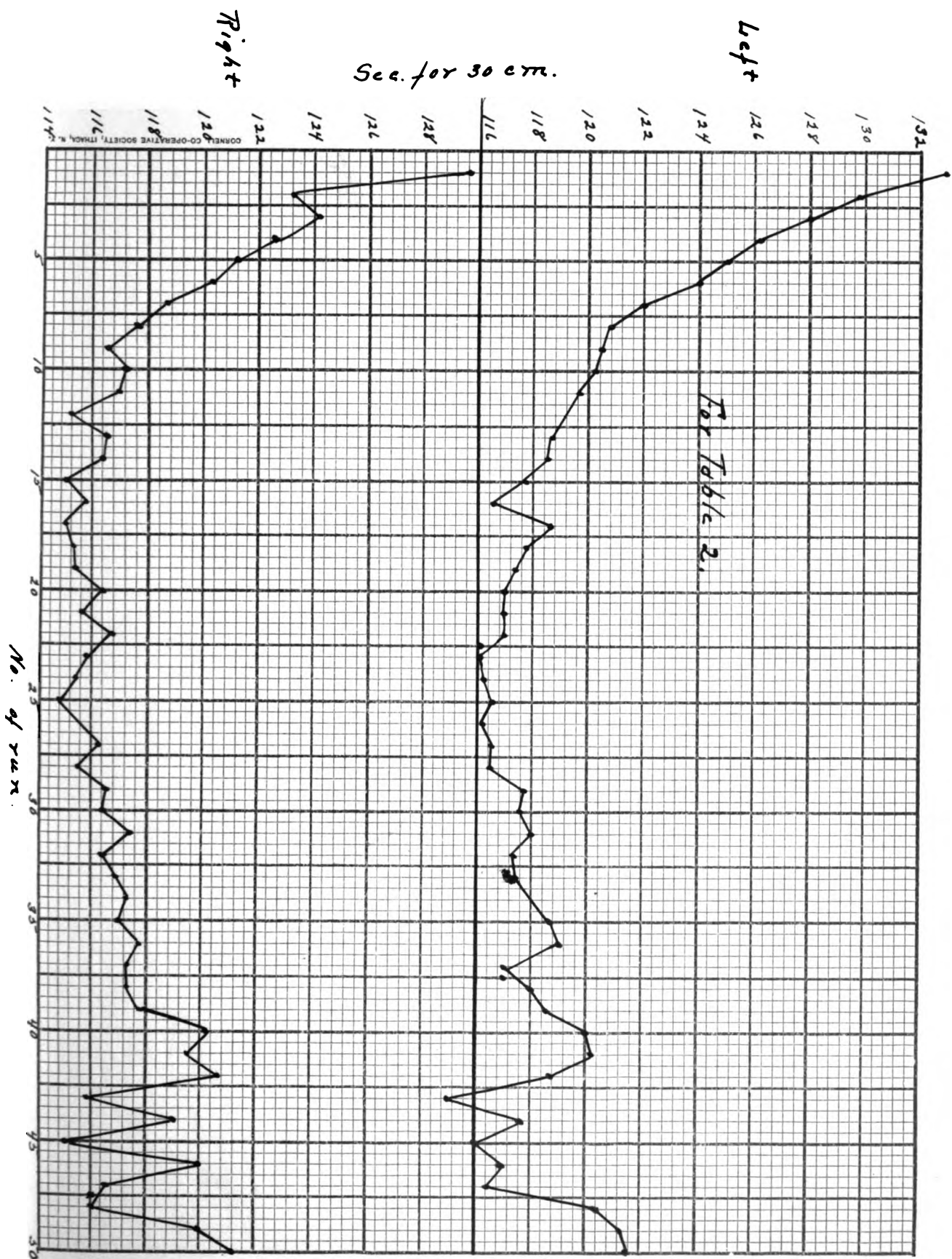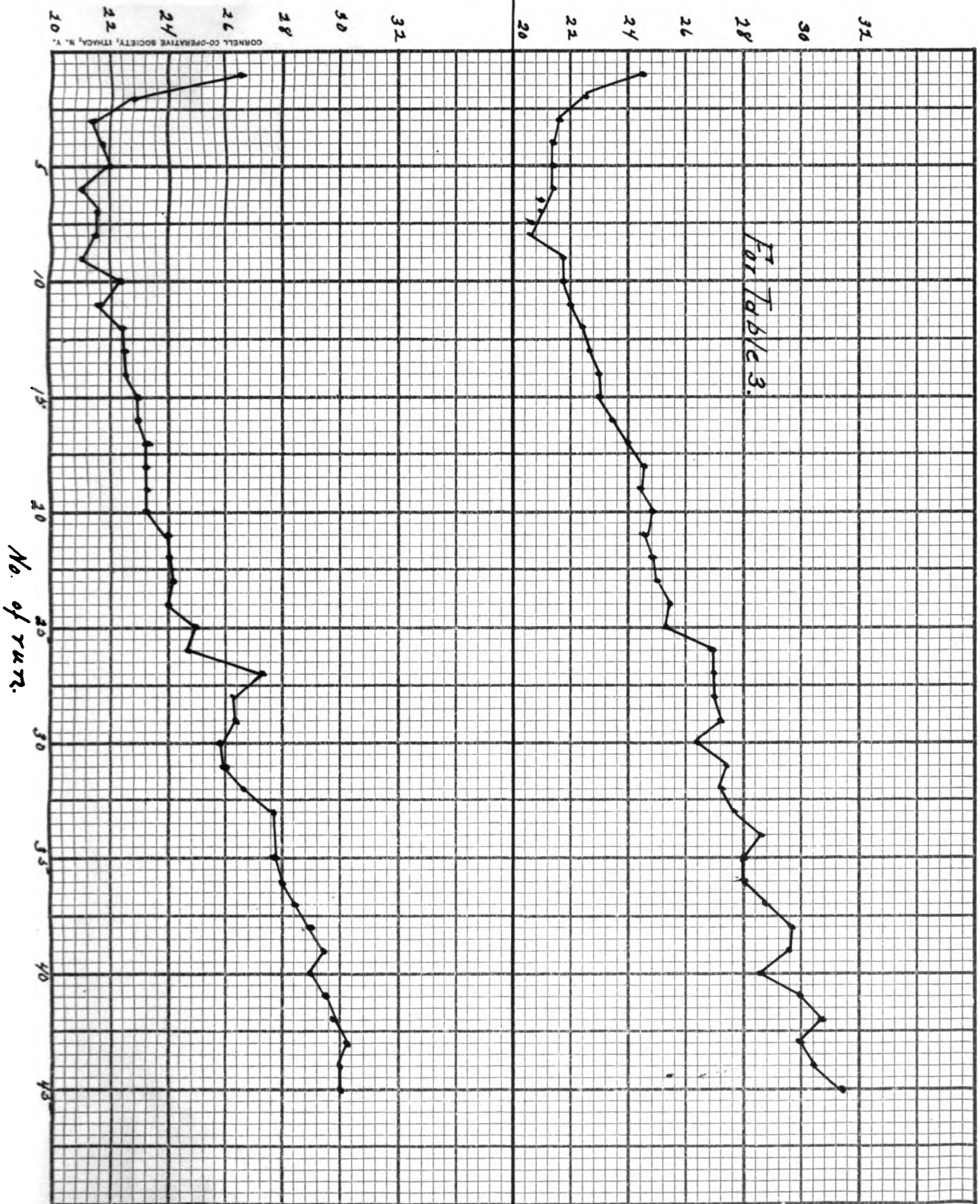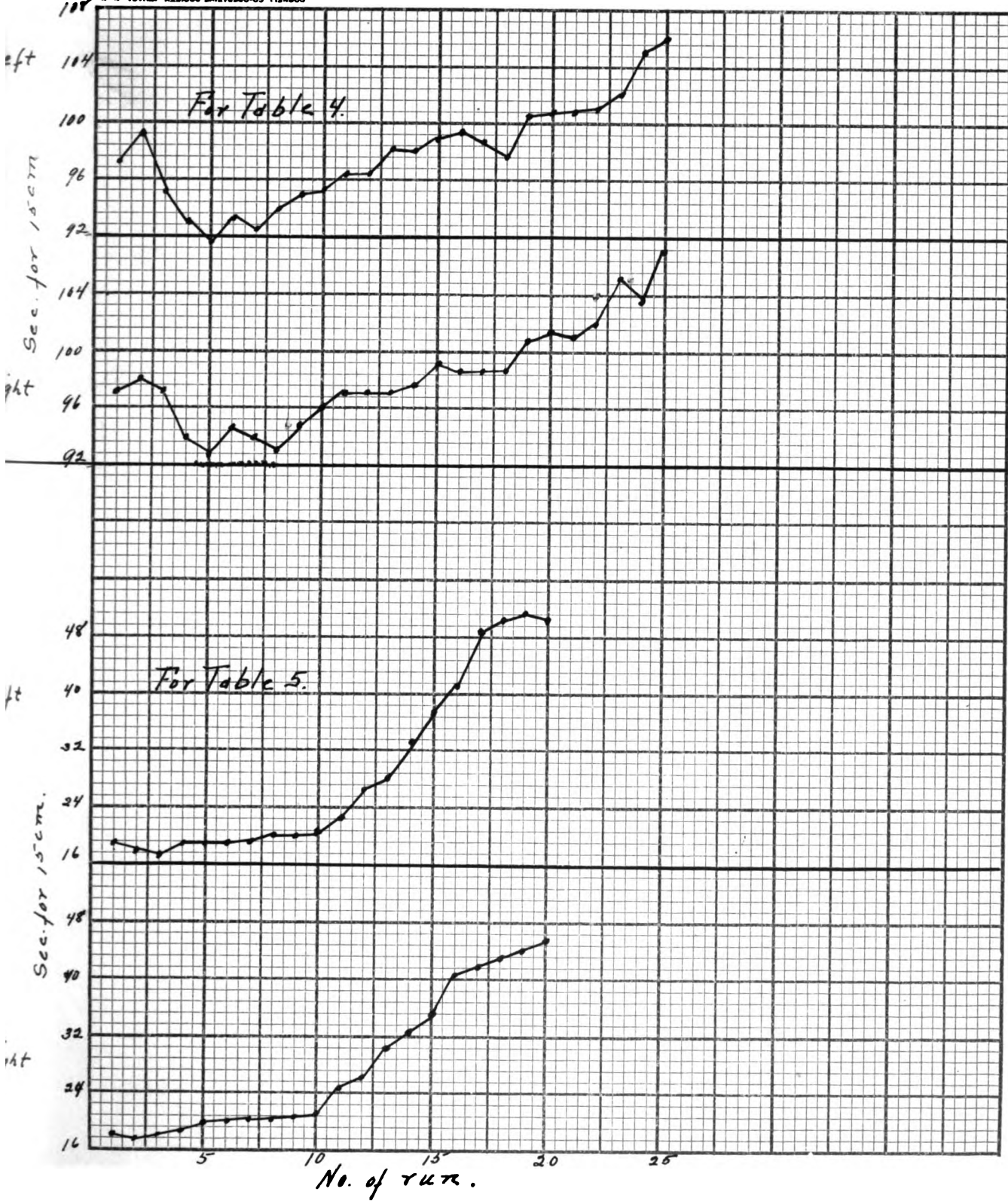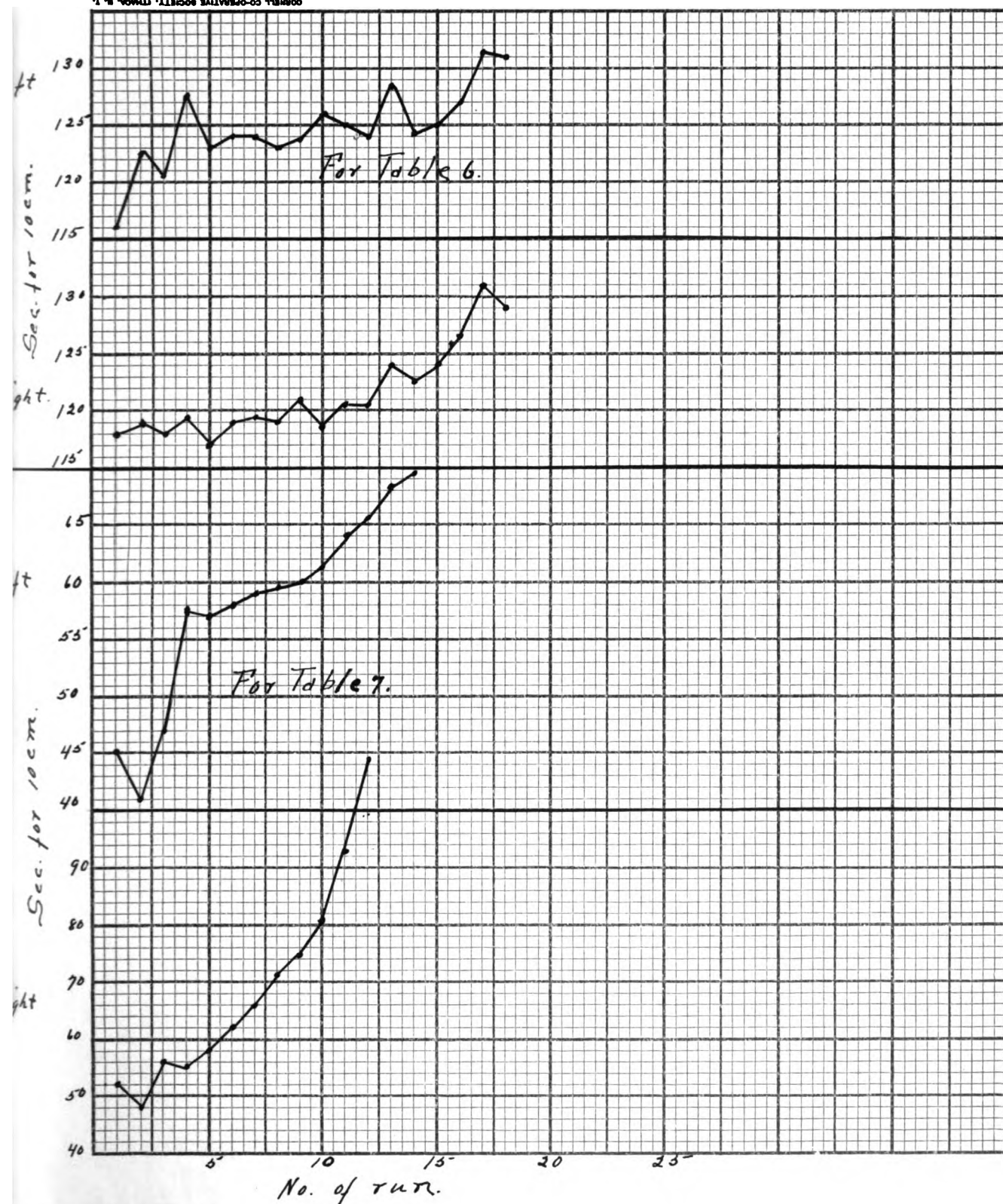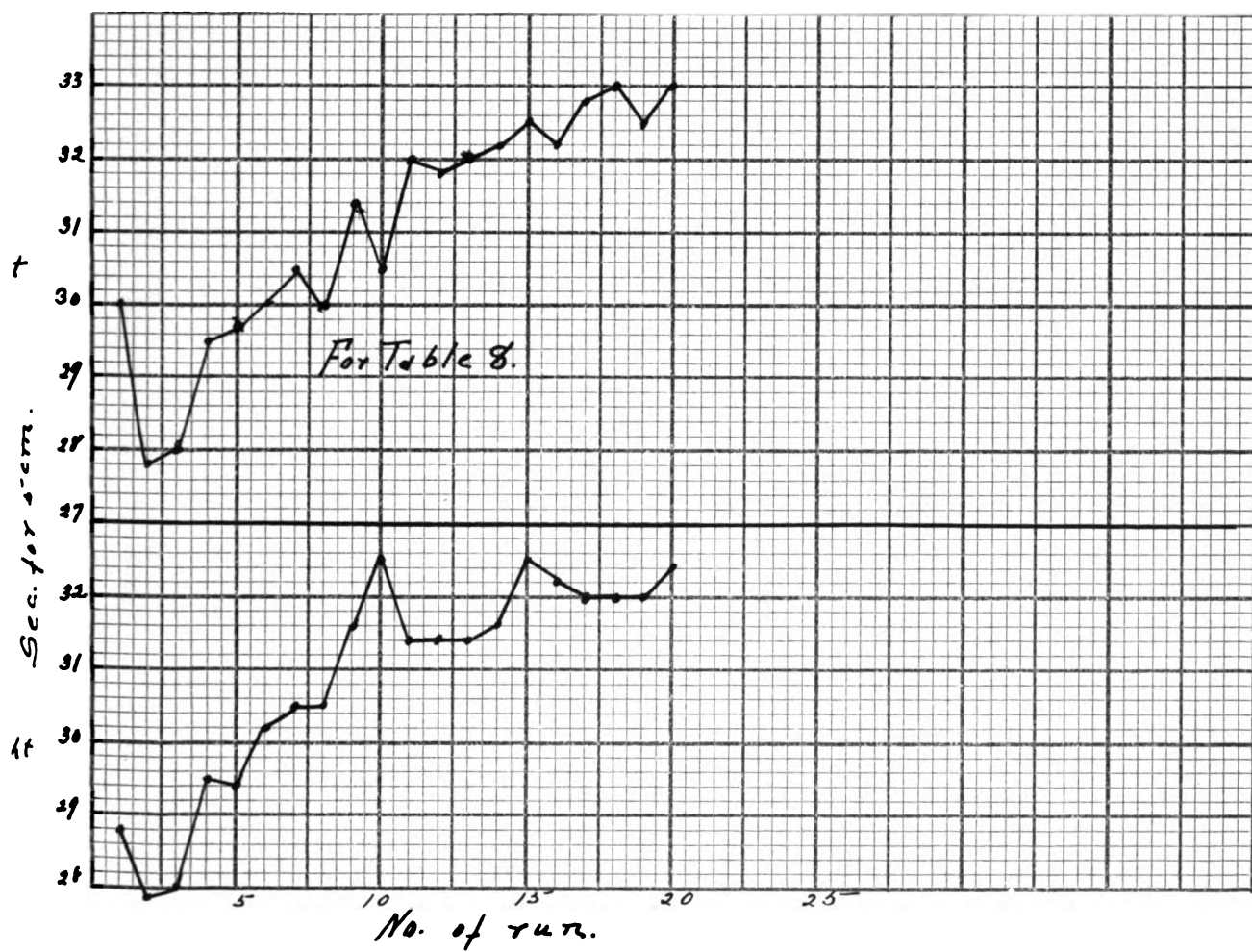
In the tables, Osmose +, is electric endosmose toward
the cathode and Osmose -, is endosmose toward the anode. This
method for distinguishing will be used throughout the paper.
The letter (L) refers to movement of the bubble toward the left
and (R) toward the right. The upper small number is the number
of the run. Thus in Table 2: 100 runs were made, 50 to the right,
and 50 to the left. A study of the tables and curves shows that
the maximum endosmose rate with water (Table 2) came only after
a long period of time. In the curve the number of the run is
plotted against the time in seconds required for the liquid to
flow a certain number of centimeters. With non aqueous solutions,
Tables 3-8, the maximum came very quickly. This difference may be in part
due to electrolysis. Water would tend to produce H and OH ions,
and as they are both highly adsorbed the maximum could only come
slowly, the OH ions being only slightly more adsorbed than the H
ions. In the case of non aqueous solvents there is always the
possibility of the production of a great number of substances.
Alcohol tends to be oxidised to acids, which, if ionised, decrease
or increase the rate depending upon subsequent adsorption and
chemical action upon the alcohol. In the case of benzaldehyde
the rapid decrease was doubtless due in large part to oxidation
from exposure to the air and the current. This produced benzoic
acid with adsorbable H ions. Also the bubble was reduced in size
by using up the oxygen contained therein, becoming so small that
the solution flowed around it and its movement did not record
the true rate. As the effect was the same (a decrease in rate)
no matter whether the original flow was + or -, it could not be

due to water getting into the apparatus. This was one of the first runs made on each solvent and only those runs averaged which were most uniform.

PRELIMINARY WORK

As preliminary to the work on non aqueous solutions, the apparatus was first tested out with water. The first apparatus used had an opening at the connectors only 3/4 of an inch in diameter and held a membrane of this size. The membrane used was cut from the bottom of a soft, fine grained battery cup. The movement was very slow. But it will be noted that from the accepted equation for endosmotic flow the volume is proportional to the size of the membrane. This suggested the apparatus as illustrated. Both of these had a three way stop cock on each chamber, like that of Briggs.[90] The left-hand stop cock in the new apparatus was found to leak and was cut out. This made the apparatus much simpler and easier to clean and fill and just as easy to get the bubble in the measuring tube. The membrane was then 32 m. m. in diameter.

Nevertheless the rate of endosmose did not materially increase and various grades of porcelain were tried unsuccessfully. Thinking this might be due to air in the membrane, it was firmly attached to a large glass tube and water sucked through for several hours with no appreciable change in the rate. It was at this point that the idea was conceived that

90. Loc. cit.

the porosity of the membrane might be the disturbing factor. Just how a change in permeability did affect the rate will form the next section of this paper.

The membranes were then built up in glass rings which had been cut from 1 1/3 inch glass tubing in sections 3 cm. long and then ground down to 2.9 cm. This was large enough in diameter so that, when fitted in between the connectors, no strain came on the cemented joints. The membranes were built up in them by suction. In a Büchner funnel was placed a piece of copper gauze and then plaster of Paris poured in around a mold in the center, leaving an opening just large enough to contain the glass rings. The ring was placed in this opening and sealed in with paraffine. A washed glass wool plug was first placed in the ring, and the membrane substance, thoroughly washed and shaken up with water, poured in, suction being applied to draw it down firmly together. Like those of Briggs[91] these were built up merely by filtering under suction. On top of this was placed another glass wool plug. Tests showed that the glass wool had no effect upon the endosmose. These membranes were kept under water until used.

A gauge was attached to the suction pump and the membranes were built up with the same weight and pressure, different weights and the same pressure, or the same weight and different pressures. The higher pressures were secured by stretching a piece of dental rubber tightly over the top and applying suction until the desired vacuum reading was attained. Membranes of asbestos and varying grades of ground and washed

91. Loc. cit.

porcelain were made up in this way, but duplication was found to be impossible and the curves of permeability vs. rate of endesmose were very irregular. (See next section.) It was then decided to try varying grades of good quantitative filter paper and this was so successful that it was used in all subsequent experiments.

To test whether stray currents around the bubble affected the flow, a rubber membrane was used and though the current was quite high (50 milliamperes) with a dilute H Cl solution, there was no movement of the bubble in thirty minutes. This could obviously not affect a reading taken in a few seconds. The length of the bubble also had no effect unless it was too small to fill the opening in the tube, when there was a tendency for the solution to creep around it. If extremely large (over 10 m.m.) it manifested greater tendency to stick.

Different size bubble tubes were tried: those of very small bore presenting difficulties due to friction and capillarity and those of very large bore being less sensitive to small rates of endosmose. The one selected had a bore of 2.5 m.m. and an average internal volume of 0.125 c.c. per cm. The distances between the electrodes was kept constant for the filter paper at 5.5 cm.

THE EFFECT OF THE PERMEABILITY OF THE MEMBRANE ON
THE RATE OF ELECTRIC ENDOSMOSE

Because this effect was a direct outgrowth of the work with water it will be considered first, with its noted regularity

also in the case of non aqueous solvents. This phenomenon
arises from the fact that as the solution is forced through
the membrane there must be a certain amount of friction and a
tendency to pile up in the electrode tube. The hydrostatic
pressure would tend to force the solution back through the
membrane as well as out into the measuring tube. If the poros-
ity of the membrane was large the back flow would be greater
than when the porosity was small as in a tightly packed mem-
brane. This would suggest that if the rate of endosmose were
plotted against the rate of permeability the result should be
a straight line. An examination of the accompanying curves
shows that in every case the rate of endosmose increases
up to a maximum and than decreases. This decrease must be
due to friction in the pores of the membrane itself.

TABLE 9

January 7, '20.

Asbestos (varying weight)   Vacuum 21 in.   Temp. 25°

Membrane No.	Voltage	Current M. M.	Bubble	Direc-tion	cm/sec Osmose	cm/sec Perme-ability	Solu-tion
2	127.5	2	2 m.m.	+	0.132	10.0	H₂O
3	127.5	1-2	5 " "	+	0.112	10.0	"
4	127.5	2	5 " "	+	0.130	5.9	"
5	127.5	3	5 " "	+	0.102	4.5	"
6	127.0	5-6	5 " "	+	0.237	3.6	"
7	127.0	2-25	6 " "	+	0.122	2.8	"
8	128.0	2-3	5.5 " "	+	0.128	2.2	"
9	128.0	2-3	6 " "	+	0.111	1.2	"
10	128.0	2-4	4 " "	+	0.128	1.1	"

TABLE 10

January 11, '20.

Asbestos vs. H_2O.

Membrane No.	Wt. Dry Asbestos	Vacuum used	Voltage	Current	Temp.	Direction	Bubble	cm/sec Osmose	cm/sec permeability
1	6 gm	5 in.	127.0	2.0 ma.	25°	+	4 m.m.	0.181	1.77
2	6 "	10 "	127.0	2-4 "	25°	+	6 " "	0.126	1.2
3	6 "	15 "	127.0	4-4.5 "	25°	+	5.5 " "	0.196	1.08
4	6 "	20 "	127.0	2-2.5 "	25°	+	5 " "	0.165	0.97
5	6 "	122 "	127.0	2.0 "	25°	+	6 " "	0.184	1.48
6	6 "	24 "	127.0	2-2.5 "	25°	+	4 " "	0.181	1.32

TABLE 11

January 13, '20.

Asbestos vs. H_2O.

Membrane No.	Wt.Dry Asbestos	Vacuum used	Voltage	Current	Temp.	Direction	Bubble	cm/sec Osmose	cm/sec permeability
1	6 gm.	5 in.	127.0	2.0	25°	+	6 m.m.	0.190	1.87
2	6 "	10 "	127.0	2.0	25°	+	6 " "	0.186	1.41
3	6 "	15 "	126.5	2.0	25°	+	6 " "	0.196	1.23
4	6 "	20 "	126.0	1.5	25°	+	6.5 "	0.193	1.04
5	6 "	22 "	117.0	1.0	25°	+	4 " "	0.190	1.65
6	6 "	24 "	117.0	1.0	25°	+	4 " "	0.184	1.41

TABLE 12

January 19, '20.

Asbestos vs H₂O.

bra-ne b.	Wt. Dry	Va- cuum used	Voltage	Current	Temp.	Di- rec- tion	Bubble	Time of Soaking	cm/sec Osmose	cm/sec permea- bility
l	6 gm.	15 in.	123.0	3-4	25°	+	5.5 m.	16.5 hrs.	0.257	1.06
l	6 "	15 "	122.0	2	25°	+	5 "	42 "	0.125	0.94
l	6 "	15 "	120.0	3-6.5	25°	+	5 "	160 "	0.380	1.11
l	6 "	15 "	122.0	2-4	25°	+	7 "	65 "	0.200	1.14
l	6 "	15 "	122.0	8	25°	+	5.5"	136 "	0.138	1.13

TABLE 13

January 22, '20.

Porcelain (40-60 mesh) vs. H₂O.

bra-ne b.	Wt. Dry	Va- cuum used	Voltage	Current	Temp.	Di- rec- tion	Bubble	Time of Soaking	cm/sec Osmose	cm/sec permea- bility
l	15 gm.	5 in.	121.0	3-5	25°	+	5.5 m.m.	17 hrs.	0.041	0.51
l	15 "	10 "	121.0	2-2.5	25°	+	7 " "	19 "	0.040	0.184
l	15 "	15 "	127.5	7-9	25°	+	6 " "	42 "	0.121	0.058
l	15 "	20 "	124.0	4	25°	+	4 " "	45 "	0.052	0.306
l	15 "	22 "	122.0	3-4.5	25°	+	7 " "	47 "	0.045	0.043
l	15 "	24 "	122.0	2-4.5	25°	+	7 " "	49 "	0.045	1.23

TABLE 14

February 2, '20.

Porcelain (100 mesh) vs. H₂O.

Mem-brane No.	Wt. Dry	Va-cuum used	Voltage	Current	Temp.	Di-rec-tion	Bubble	Time of Soaking	cm/sec Osmose	cm/sec permea-bility
	5 gm.	15 in.	128.5	6-11	25°	+	7 m.m.	23 hrs.	0.038	Too Rapid
	5 "	15 "	128.5	2-4	25°	+	7 " "	24 "	0.065	1.87
	10 "	15 "	128.5	4	25°	+	3 " "	27 "	0.174	0.79
	10 "	15 "	128.5	2	25°	+	4 " "	29.5 "	0.083	0.656
	15 "	15 "	128.5	2	25°	+	3 " "	45.5 "	0.101	0.670
	15 "	15 "	128.0	16	25°	+	7 " "	118 "	0.390	0.610
	20 "	15 "	128.0	8-10	25°	+	4 " "	119.5 "	0.233	0.142

TABLE 15

February 9, '20.

Porcelain (100 mesh) vs H₂O.

Mem-brane No.	Wt. Dry	Va-cuum used	Voltage	Current	Temp.	Di-rec-tion	Bubble	Time of Soaking	cm/sec Osmose	cm/sec permea-bility
	15 gm.	5 in.	128.0	(3-20)	25°	+	5 m.m.	42 hrs.	0.078	4.34
	15 "	10 "	128.0	3-16	25°	+	7 " "	47 "	0.051	4.21
	15 "	15 "	128.0	2	25°	+	5 " "	90 "	0.096	4.65
	15 "	20 "	128.0	1- 2	25°	+	5 " "	138 "	0.074	2.96
	15 "	22 "	128.0	1- 1.5	25°	+	5 " "	140 "	0.087	3.25
	15 "	24 "	128.0	1- 2	25°	+	5 " "	143 "	0.056	4.57

TABLE 16

February 26, '20.

Filter Paper vs H$_2$O.

m-rane No.	No. of thick-ness	Kind	Voltage	Current	Temp.	Di-rec-tion	Bubble	cm/sec Osmose	cm/sec permea-bility
1		S.& S. No.597	127.5	4-8	25°	+	6 m.m.	0.015	7.0
2		" "	127.5	2	"	+	6 " "	0.049	2.61
3		" "	127.5	2-2.5	"	+	5.5 "	0.096	1.95
4		" "	127.5	2-3	"	+	3 " "	0.106	1.42
5		" "	127.5	2-4	"	+	3 " "	0.099	1.12
6		" "	127.5	3-4	"	+	4 " "	0.098	0.56
7		" "	127.5	4	"	+	5 " "	0.113	0.54
8		" "	127.0	3-6	"	+	5 " "	0.142	0.41
9		" "	129.5	2-4	"	+	3 " "	0.093	0.50
10		" "	129.5	3-4	"	+	3 " "	0.076	0.63
11		" "	129.5	3-4	"	+	4 " "	0.093	0.66
12		" "	129.5	3-4	"	+	5 " "	0.087	0.54
13		" "	129.0	5-7	"	+	2 " "	0.073	0.51
14		" "	127.5	2-2.5	"	+	3 " "	0.033	0.23

TABLE 17

March 2, '20.

Filter Paper vs H₂O.

Membrane No.	No. of thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec permeability	Membrane after run
	4	S.& S. No.590	120.0	2	+	25°	5.m.m.	0.053	0.34	tiny air bubbles
	8	" "	120.5	2	+	"	5 " "	0.062	0.28	O.K.
	12	" "	120.5	2	+	"	6 " "	0.060	0.18	(air (bubbles
	16	" "	120.5	2	+	"	4 " "	0.027	0.10	O.K.
	20	" "	120.5	1	+	"	5 " "	0.025	0.075	O.K.
	2	" "	120.5	1	+	"	2.5 "	0.034	0.69	(tiny air (bubbles

TABLE 18

March 4, '20.

Filter Paper vs. H₂O.

Membrane No.	No. of thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec permeability	Membrane after run
1	2	S.& S. No.589	122.5	1	+	25°	6 m.m.	0.032	5.63	O.K.
2	4	" "	122.5	1	+	"	3 " "	0.054	2.64	O.K.
3	8	" "	122.5	1	+	"	3 " "	0.081	1.11	O.K.
4	12	" "	127.0	1	+	"	4 " "	0.055	0.64	O.K.
5	16	" "	117.0	1	+	"	4 " "	0.048	0.25	O.K.
6	20	" "	117.0	1	+	"	6 " "	0.040	0.20	O.K.

TABLE 19

March 9, '20.

Filter Paper vs. H_2O.

Membrane No.	No. of thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec permeability	Membrane after run
1	2	S.& S. No.595	115.5	1	+	25°	4 M.M.	0.035	6.66	O.K.
2	4	" "	115.5	1	+	"	3 " "	0.058	3.44	O.K.
3	8	" "	130.0	1-1.5	+	"	5 " "	0.063	1.02	O.K.
4	12	" "	130.0	1.5	+	"	4 " "	0.062	0.82	O.K.
5	16	" "	133.5	1-2	+	"	5 " "	0.032	0.76	O.K.
6	20	" "	130.0	1-2	+	"	3.5 "	0.029	0.65	O.K.

TABLE 20

March 11, '20.

Filter Paper vs. H_2O.

Membrane No.	No. of thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec permeability	Membrane after run
1	2	Whatman No. 40	130.0	1	+	25°	5 M.M.	0.051	4.81	O.K.
2	4	" "	122.5	1	+	"	3 " "	0.071	2.28	O.K.
3	8	" "	122.0	1-1.5	+	"	3.5 "	0.074	1.02	O.K.
4	12	" "	130.0	1-2	+	"	5 " "	0.077	0.66	(one layer (cracked
5	16	" "	130.0	2-4	+	"	4.5 "	0.061	0.45	"
6	20	" "	130.0	2	+	"	5 " "	0.041	0.39	"

TABLE 21

March 15, '20.

Filter Paper vs. H₂O.

Membrane No.	No. of thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec permeability	Membrane after run
1	2	Ordinary	129.0	2	+	25°	6 m.m.	0.030	3.63	O.K.
2	4	"	129.5	2	+	"	3 " "	0.041	1.33	tiny bubble
3	8	"	129.5	2	+	"	3.5 "	0.043	0.66	O.K.
4	12	"	129.0	2-3	+	"	5 " "	0.031	0.53	Ruptured M. G.
5	16	"	129.0	2-3	+	"	4 " "	0.042	0.35	O.K.
6	20	"	129.0	4-6	+	"	5 " "	0.031	0.28	O.K.

TABLE 22

April 10, '20.

Acetone vs. S. & S. Paper No. 589.

Membrane No.	No. of thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec permeability
1	2	Acetone	406.5	0	+	25°	6 m.m.	1.081	26.5×10^{-4}	8.88
2	4	"	"	0	+	"	6 " "	2.459	60.4X "	1.32
3	8	"	"	0	+	"	6 " "	2.288	56.2X "	0.84
4-A	12	"	"	0	+	"	7 " "	2.255	55.6X "	1.77
4-B	12	"	"	0	+	"	8 " "	1.925	47.3X "	1.11
5	16	"	"	0	+	"	6 " "	1.152	28.4X "	0.82
6	20	"	"	0	+	"	5 " "	1.333	32.7X "	0.96

TABLE 23

May 12, '20.

Amyl Alcohol vs. S. & S. Paper No. 589.

Run No.	No.of thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec permeability
1	2	Amyl Alcohol	623.0	0	-	25°	3.5 m.m.	0.124	1.9×10^{-4}	0.56
2	4	"	"	0	-	"	5 " "	0.154	2.4X "	0.22
3	8	"	"	0	-	"	5.5 " "	0.128	2.0X "	0.16
4	12	"	"	0	-	"	4.5 " "	0.091	1.4X "	0.11
5	16	"	"	0	-	"	4.5 " "	0.073	1.1X "	0.087

TABLE 24

May 31, '20.

Nitro Benzene vs. S. & S. Paper No. 589.

Run No.	No.of thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec permeability
1	2	Nitro Benzene	555.0	0	+	25°	3 m.m.	0.182	3.2×10^{-4}	2.57
2 from previous	4	"	"	0	+	"	5 " "	0.267	4.8X "	1.35
	6	"	"	0	+	"	4.5 " "	0.391	7.0X "	0.88
3	8	"	"	0	+	"	6 " "	0.725	13.0X "	0.68
4	12	"	"	0	+	"	4 " "	0.748	13.4X "	0.50
5	16	"	"	0	+	"	3 " "	0.627	11.2X "	0.38

TABLE 25

June 11, '20.

Pyridine vs. S. & S. Paper No. 589.

Run No.	No.of Thick-ness	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec permea-bility
1	2	Pyri-dine	971.0	0.5	+	26.5°	4.5 m.m.	0.201	20.7X10^{-4}	4.00
2	4	"	"	0.5	+	"	5 " "		0.122	12.5X "	1.76
3	8	"	"	0.5	+	"	5 " "		0.110	11.3X "	1.12
4	12	"	"	0.5	+	"	3.5 " "		0.089	9.1X "	0.68
5	1	"	"	0.5	+	"	4 " "		0.069	7.1X "	10.00

TABLE 26

June 21, '20.

Benzaldehyde vs. S. & S. Paper No. 589.

Run No.	No.of Thick-ness	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec.volt Osmose	cm/sec Permea-bility
1	2	Benzal-dehyde	954.0	0.5	+	25°	4.5 m.m.	0.128	13.3X10^{-5}	3.74
2	4	"	"	0.5	+	"	3 " "		0.156	16.3X "	1.76
3	8	"	"	0.5	+	"	3.5 " "		0.223	23.3X "	0.79
4	12	"	"	0.5	+	"	3.5 " "		0.306	32.0X "	0.56
5	16	"	"	0.5	+	"	3.5 " "		0.288	30.1X "	0.45
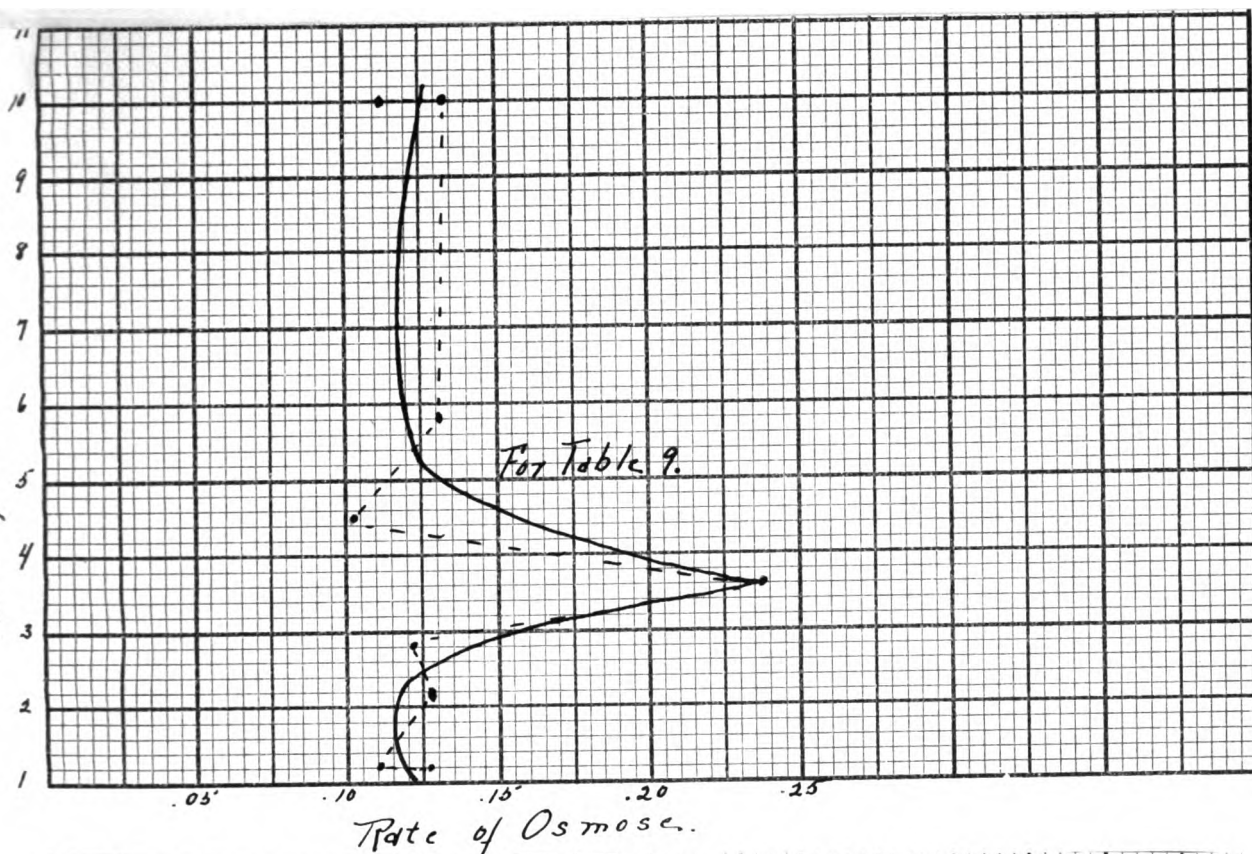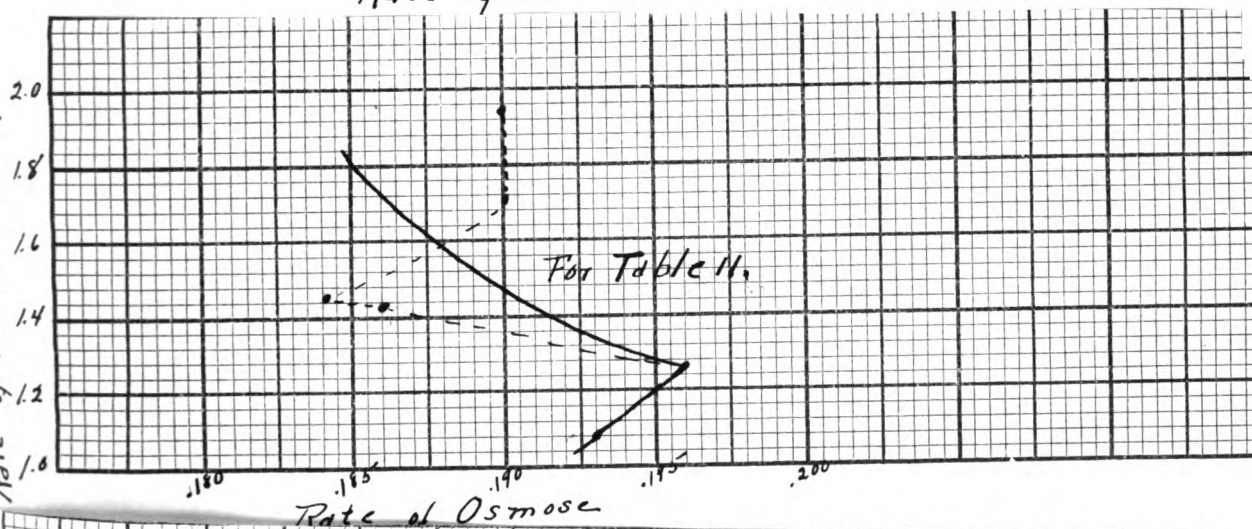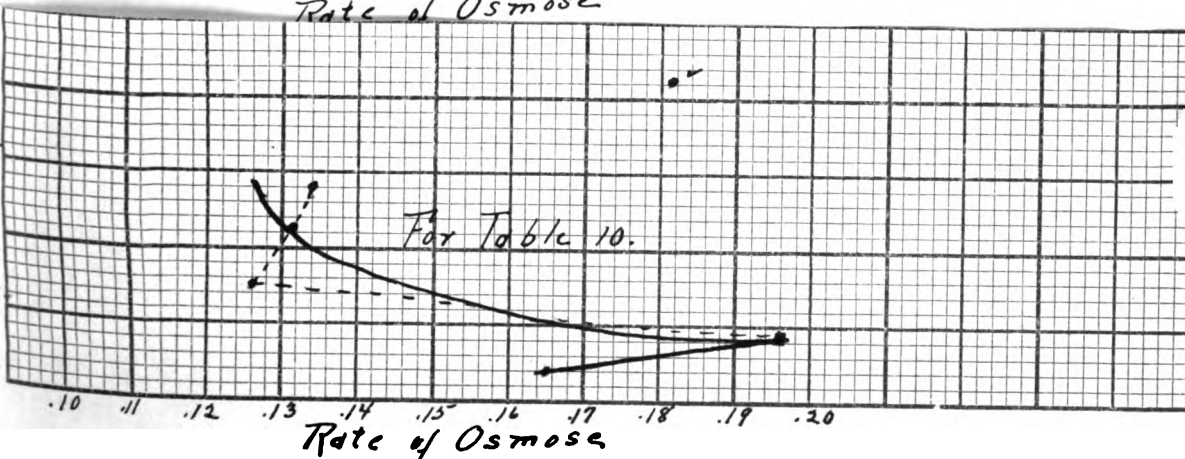
For Table 9.

Rate of Permeability

Rate of Osmose.

For Table 11.

Rate of Permeability

Rate of Osmose

For Table 10.

Rate of Osmose

For Table N_1

Rate of Permeability

2.0
1.8
1.6
1.4
1.2
1.0

.180   .185   .190   .195   .200

Rate of Osmose

For Table 12.

For Table 13.

For Table 14.

For Table 15.

For Table 16.

Rate of Permeability.

Rate of Osmose

For Table 17.

Rate of Permeability

Rate of Osmose

For Table 18.

Rate of Permeability.

Rate of Osmose.

For Table 19.

Rate of Osmose

For Table 20.

Rate of Osmose

For Table 21.

Rate of Osmose

For Table 22.

Rate of Osmose

For Table 23.

Rate of Osmose

For Table 24.

Rate of Osmose.

For Table 25.

For Table 26.

For Table 27.
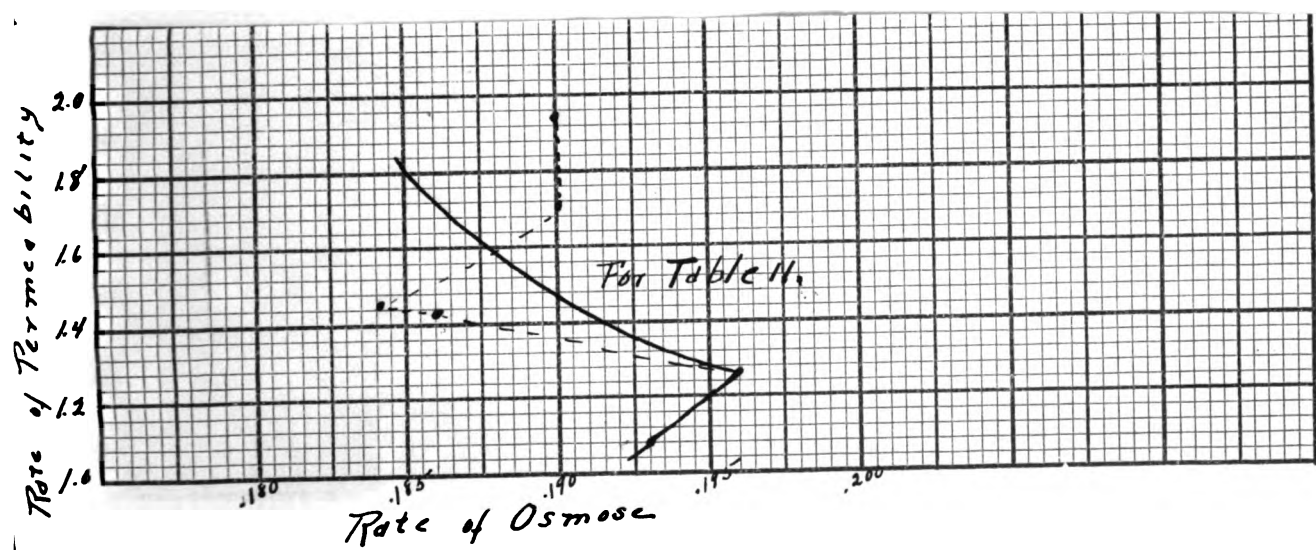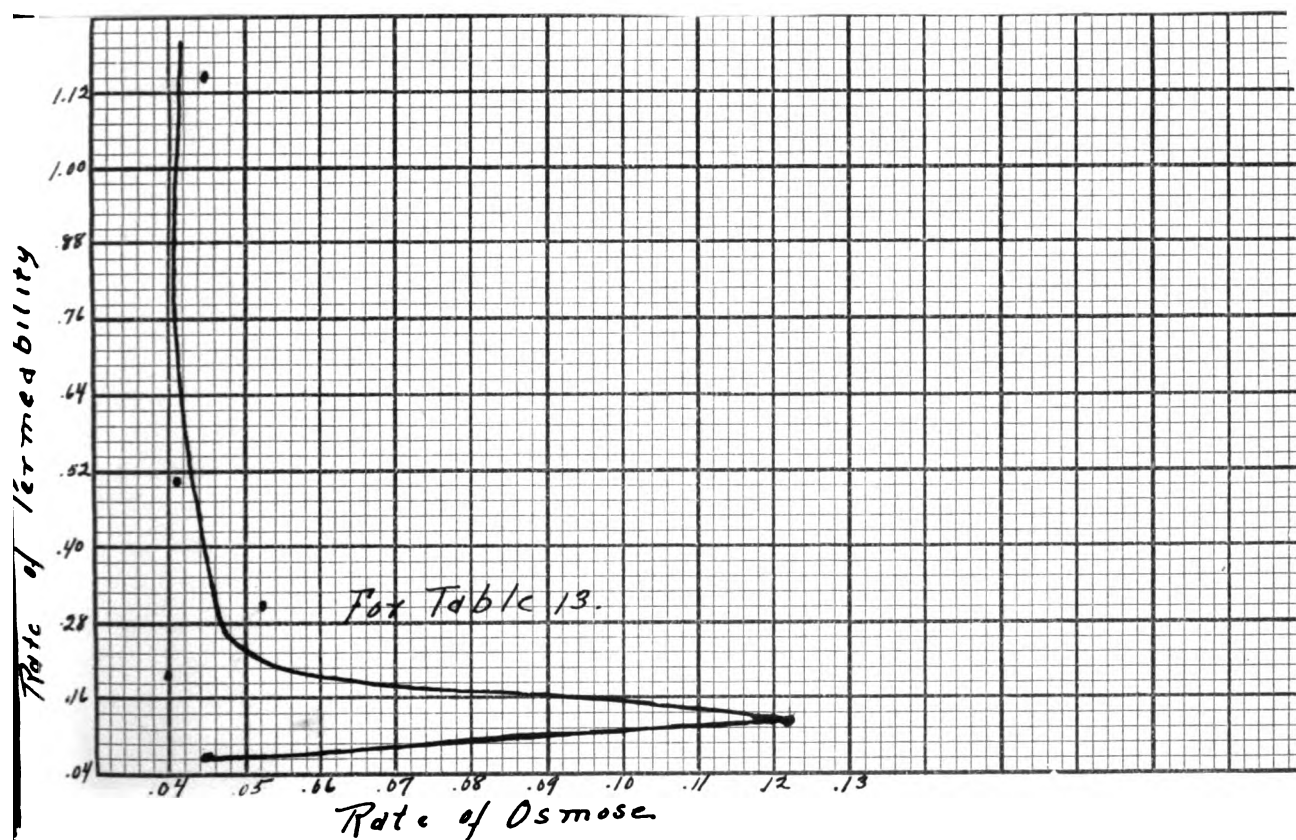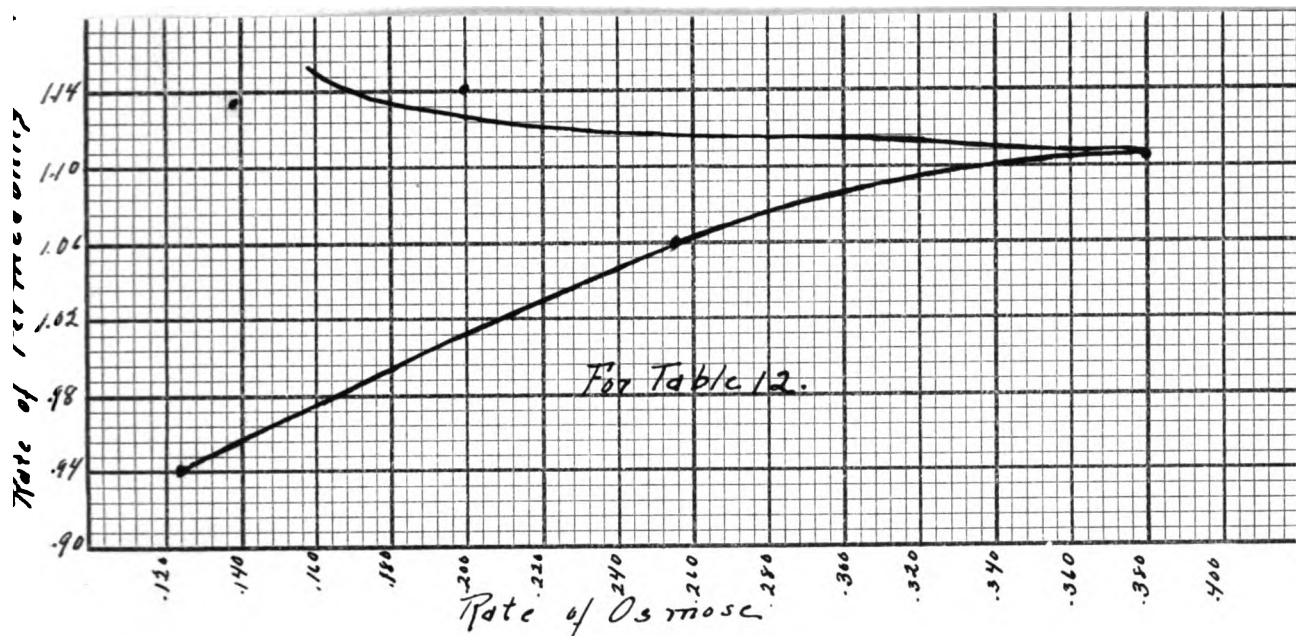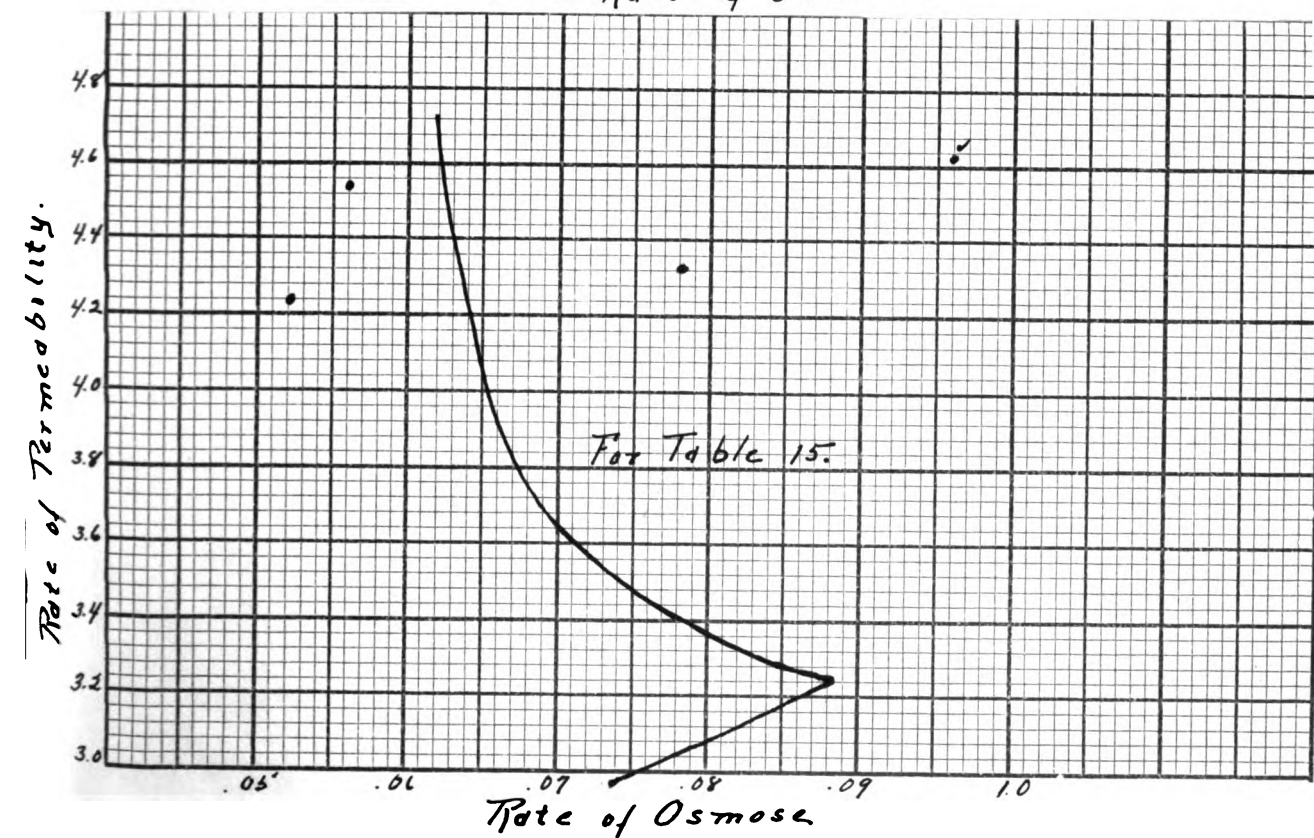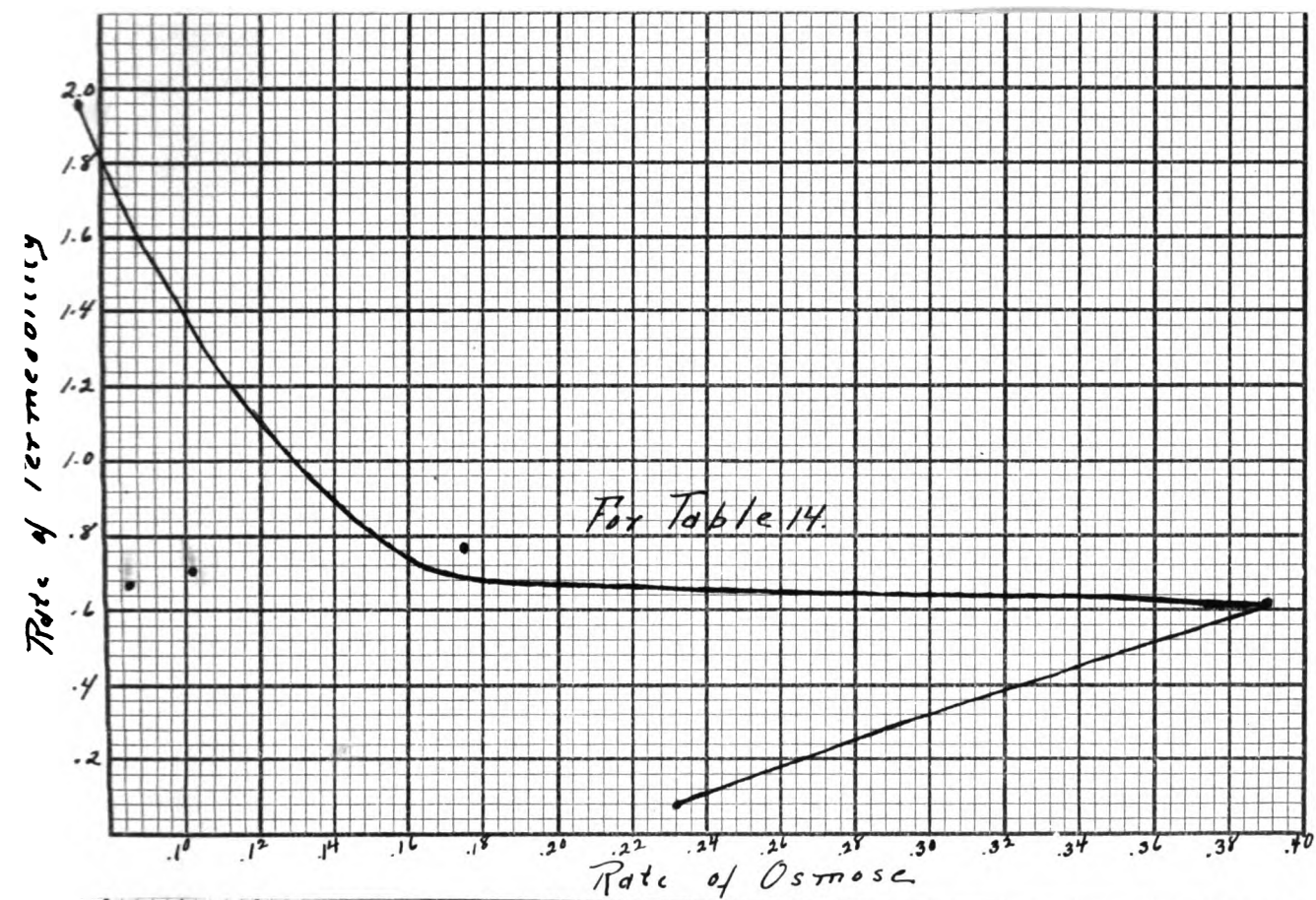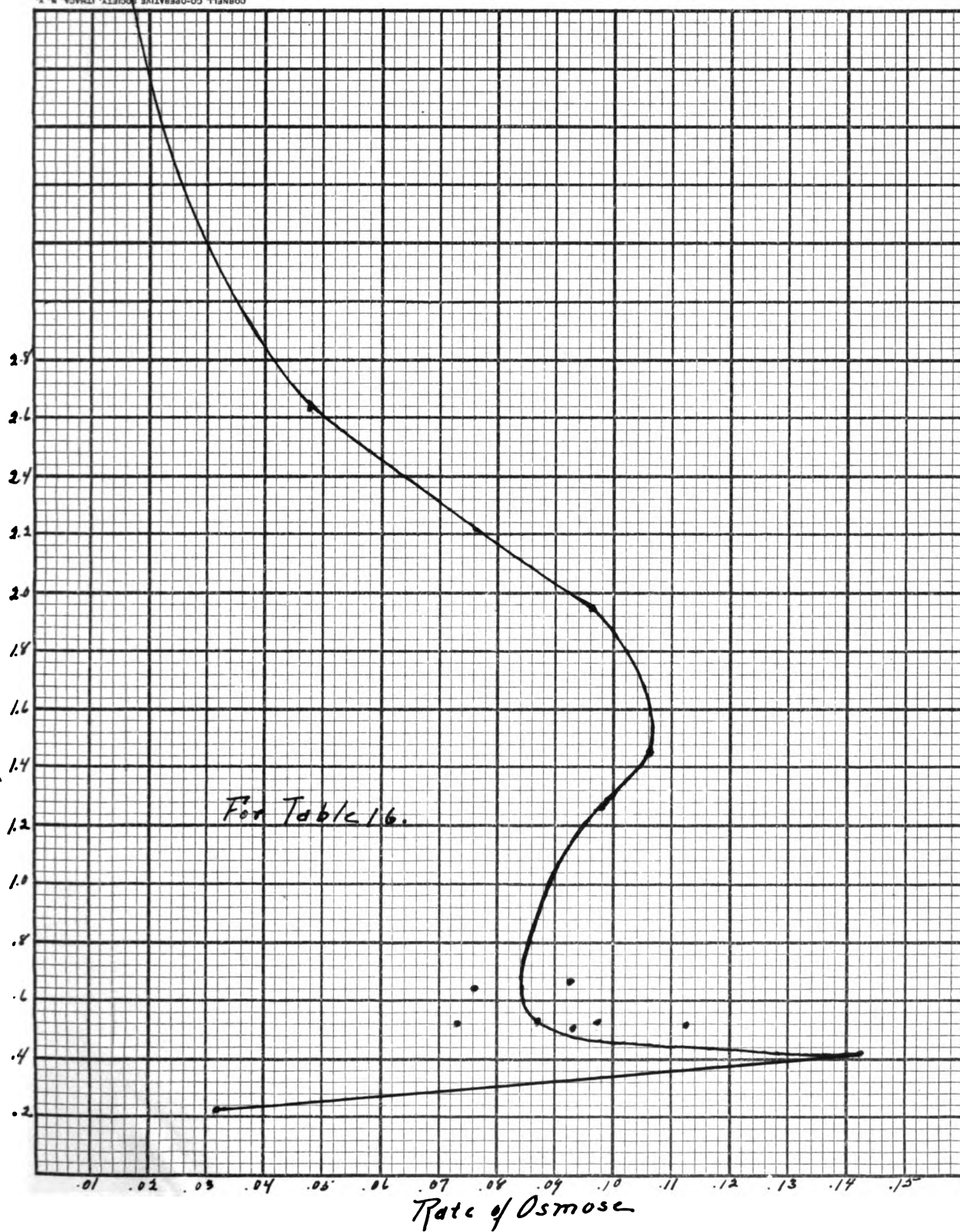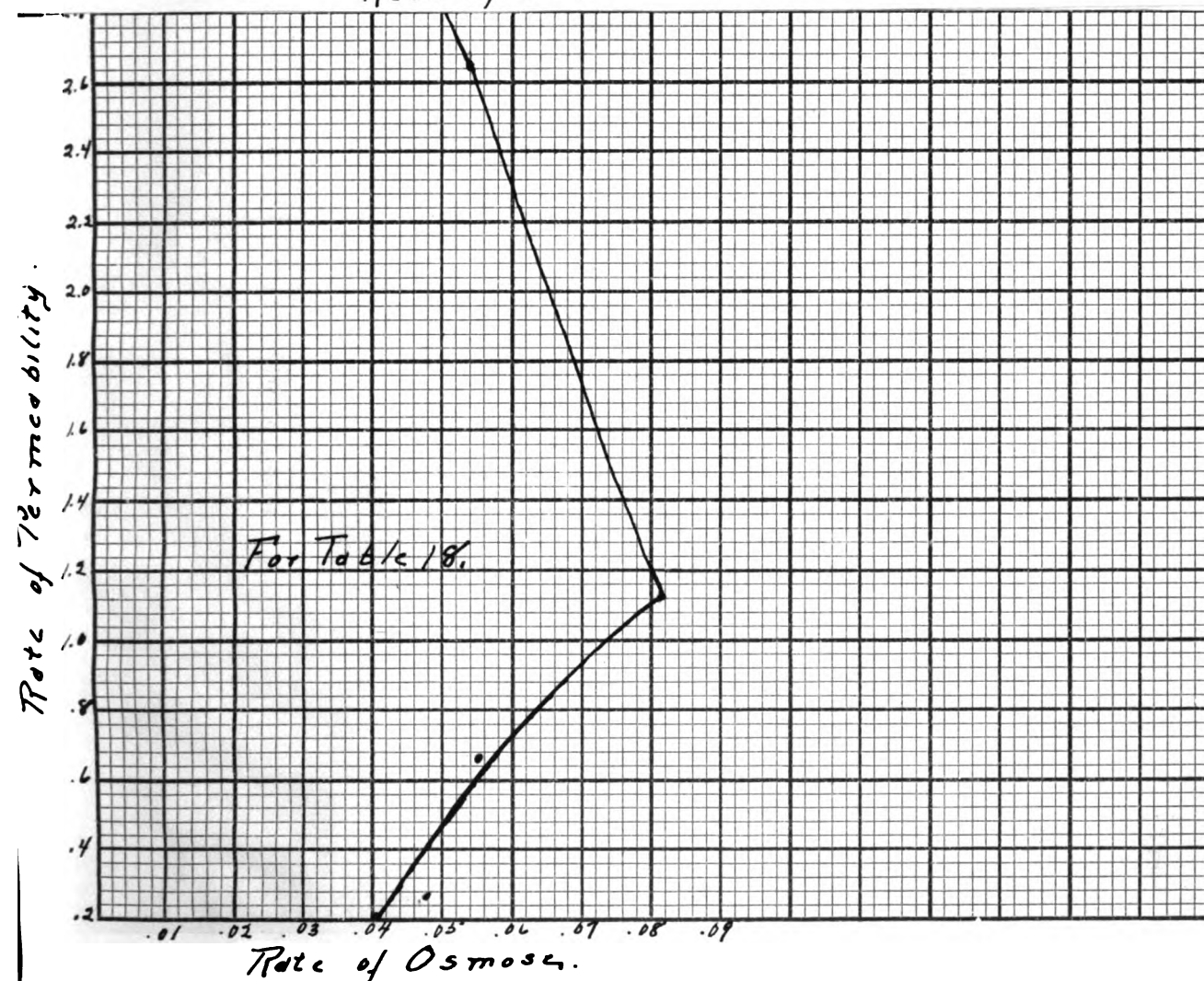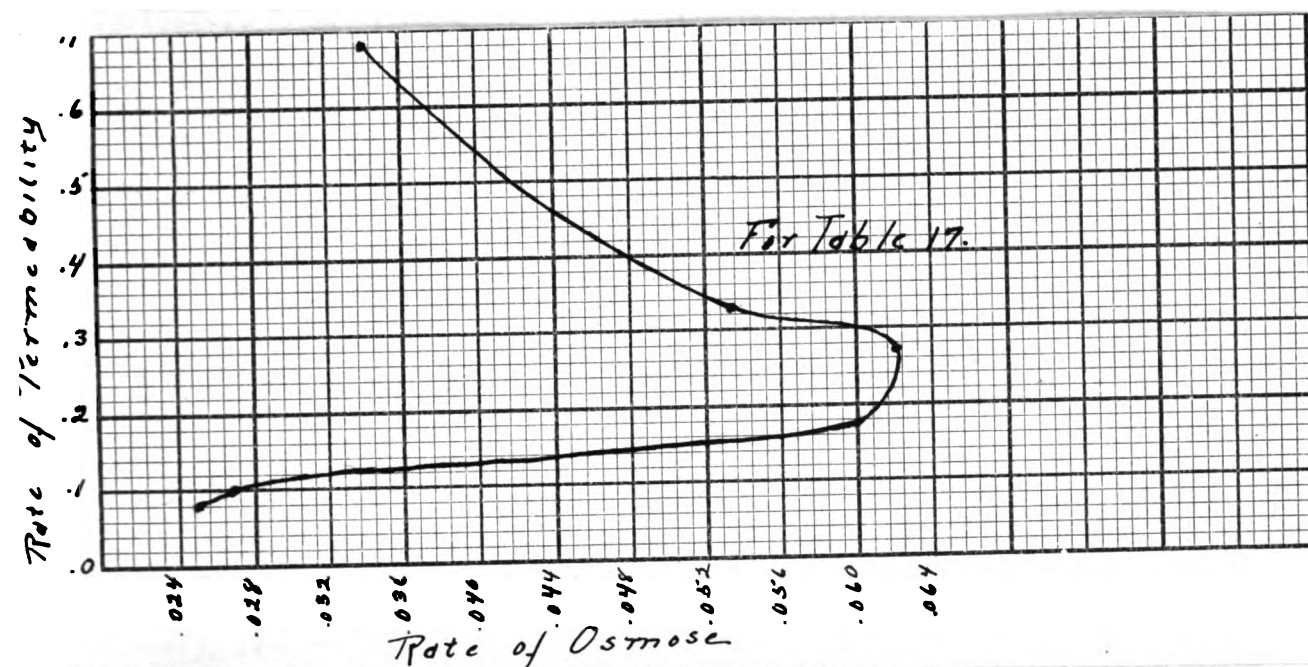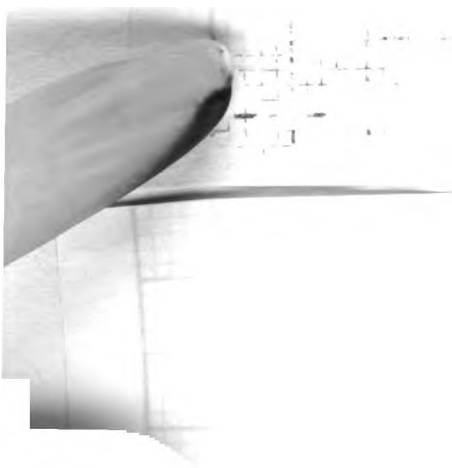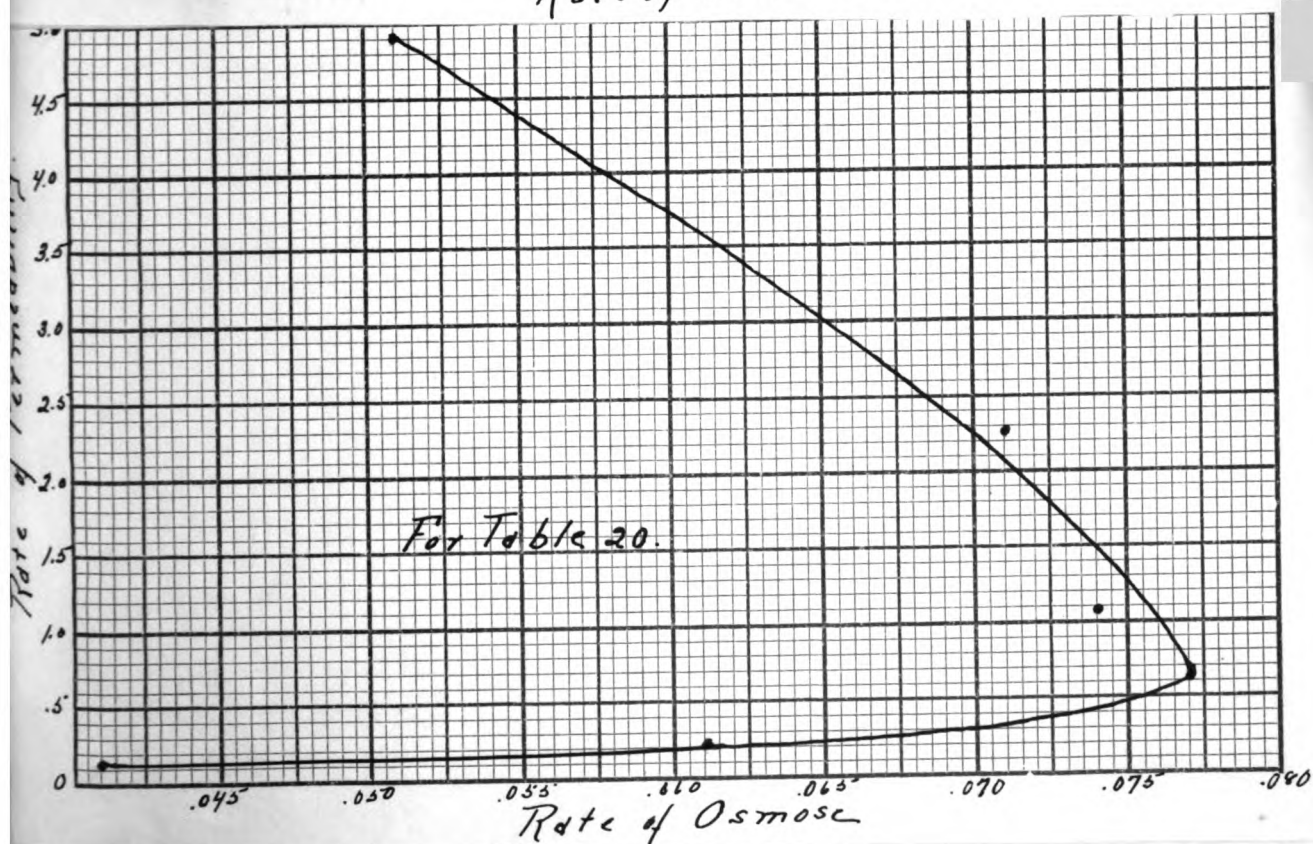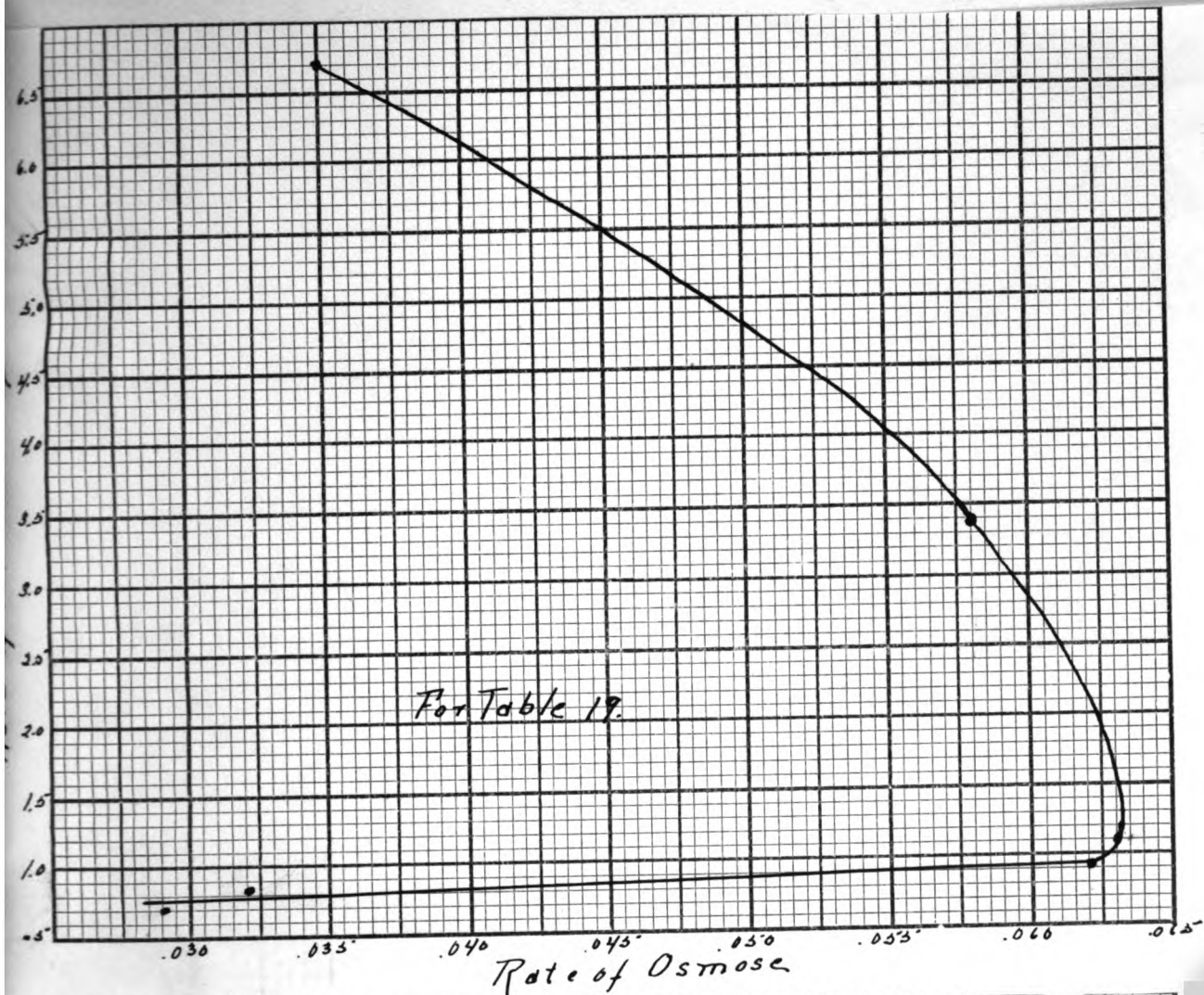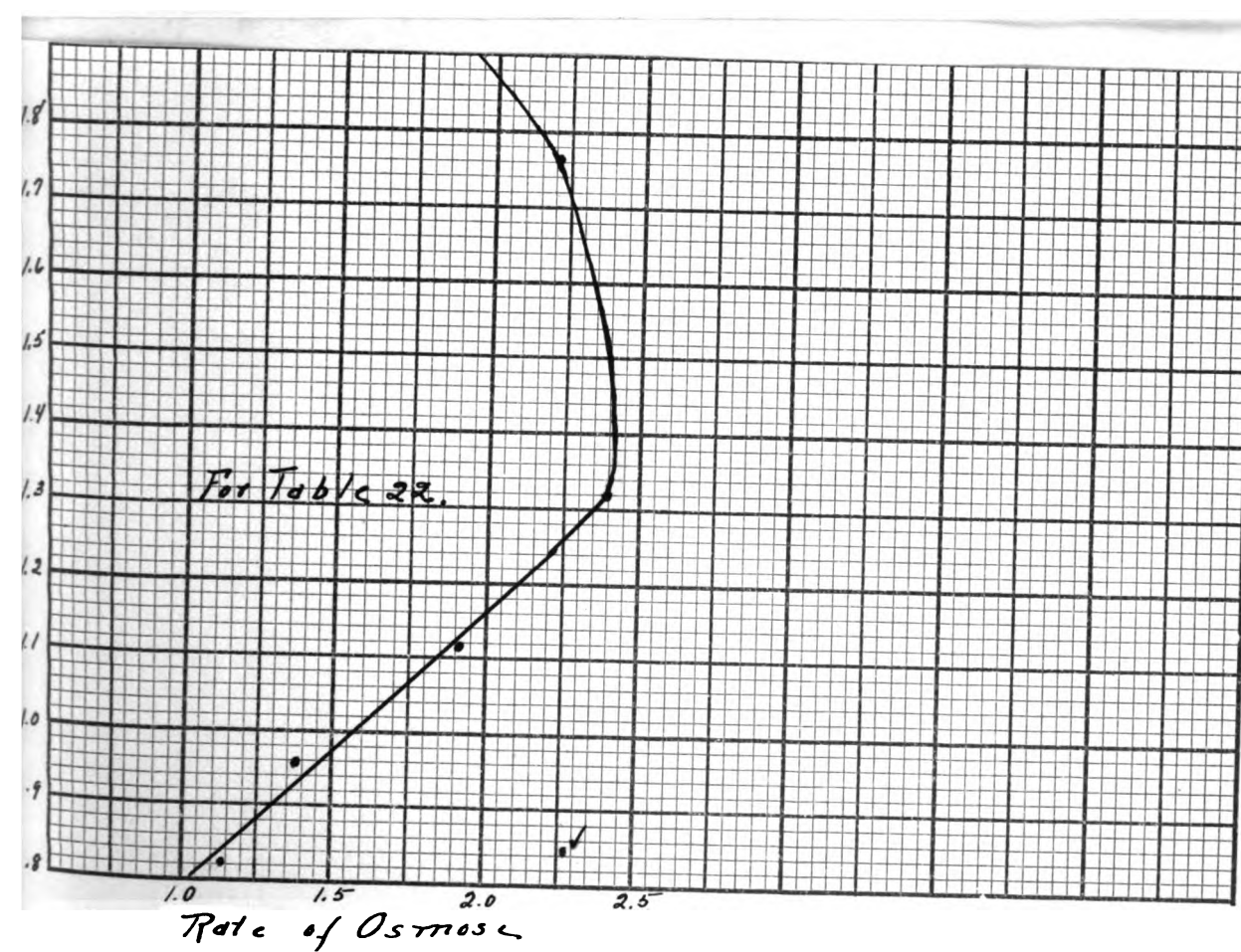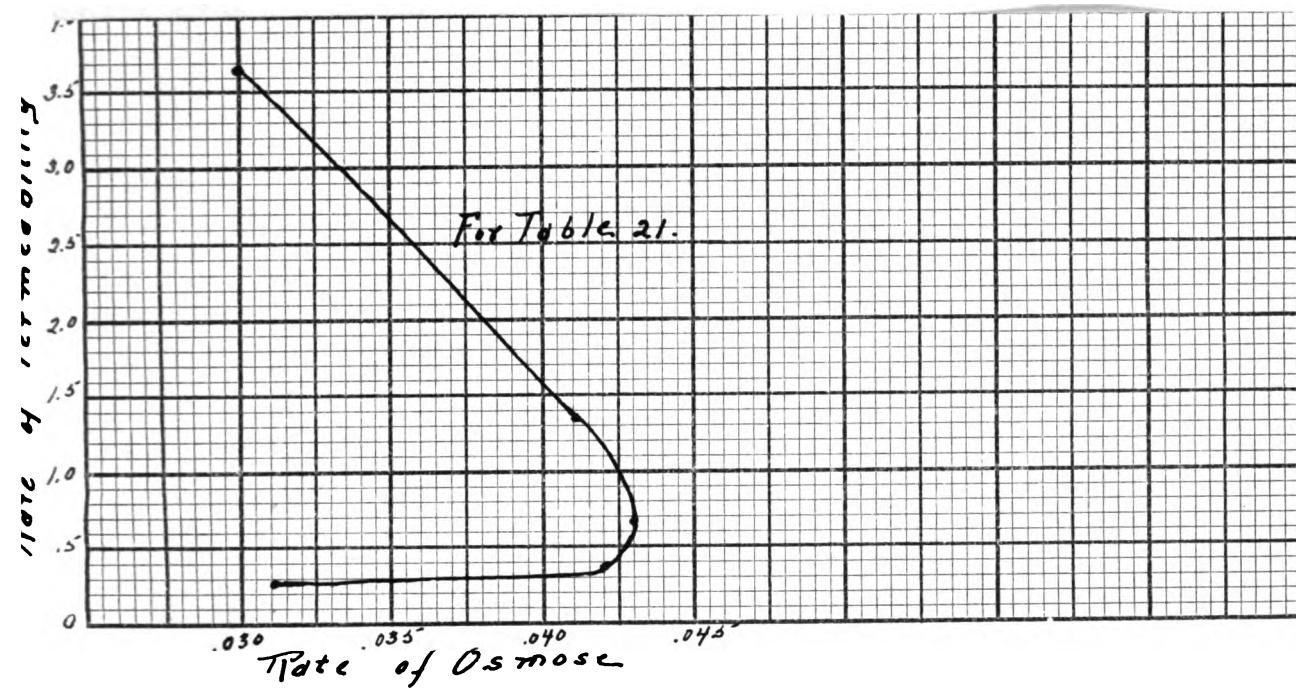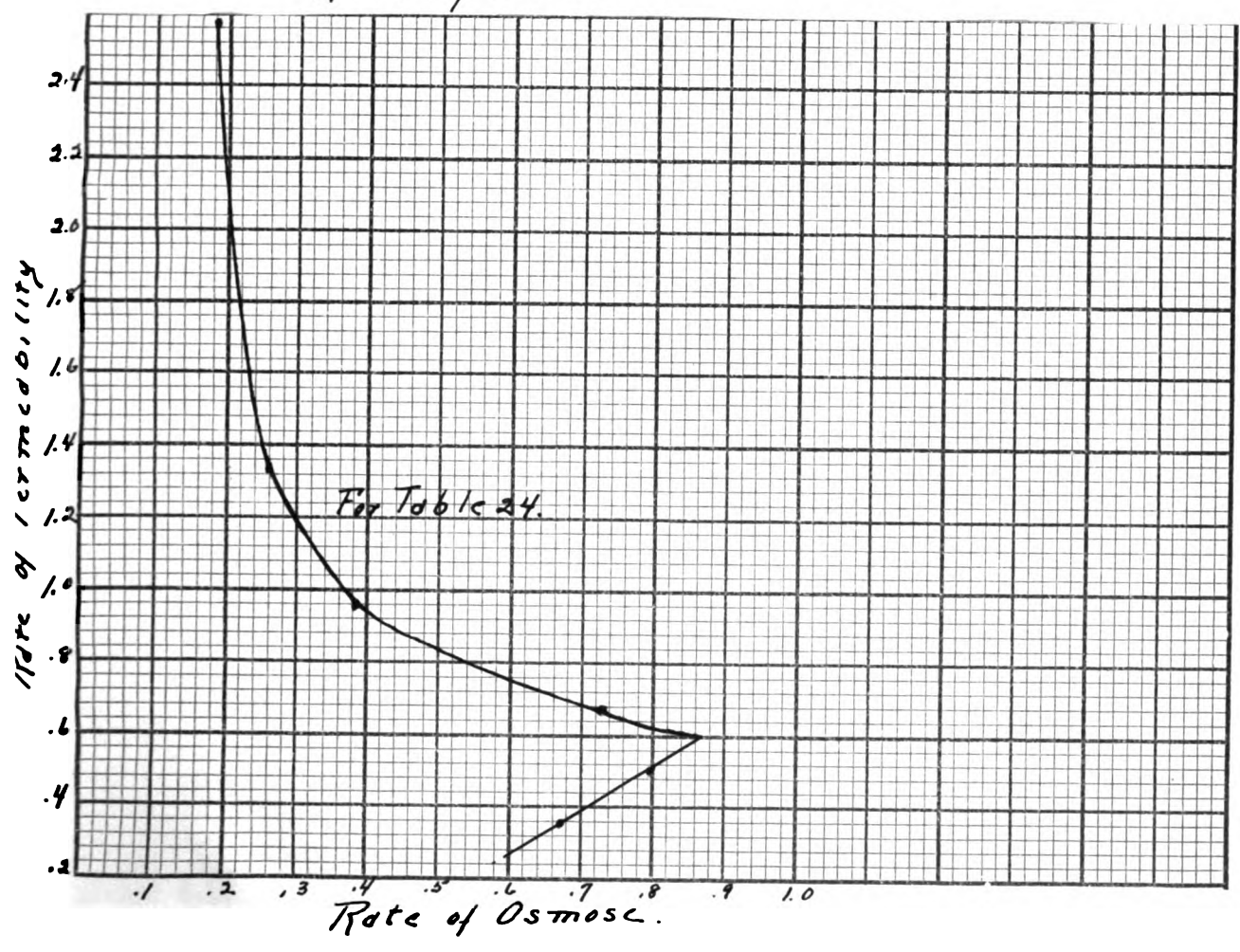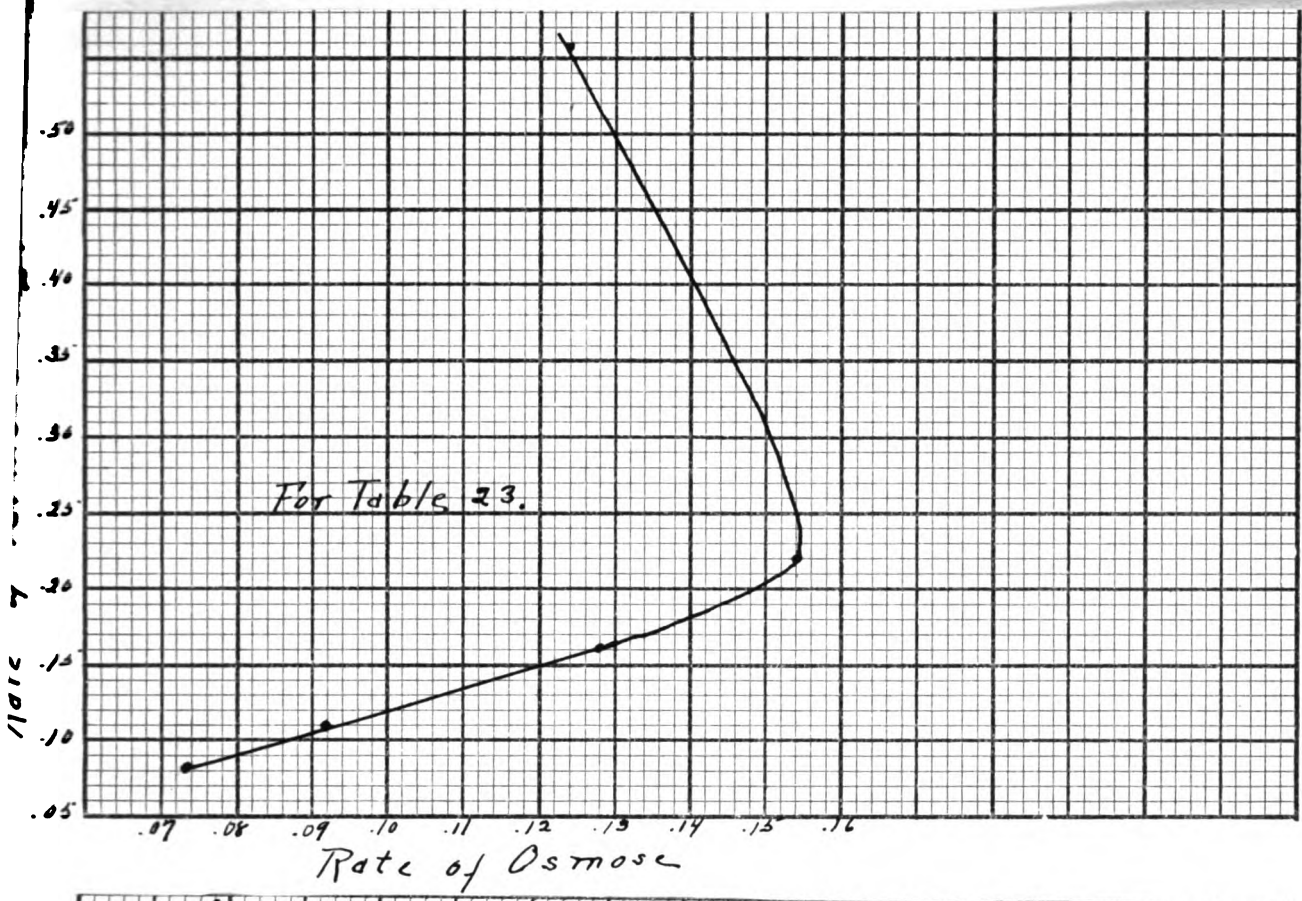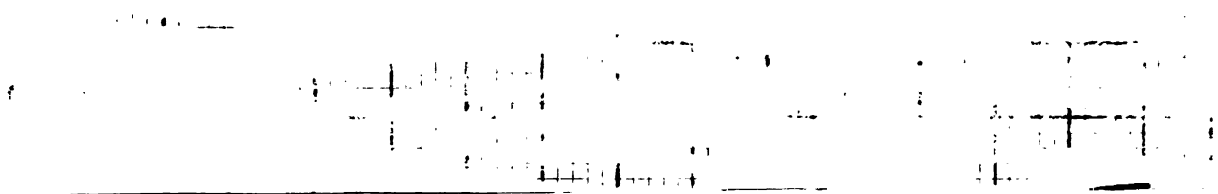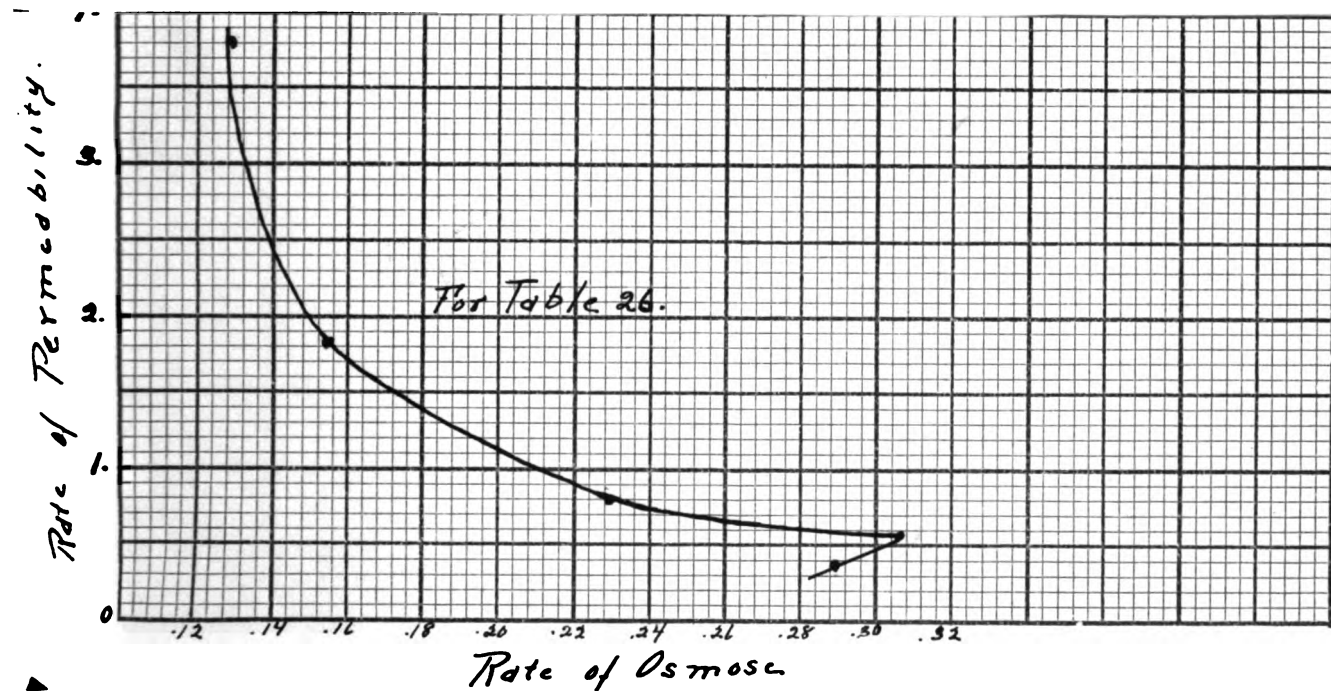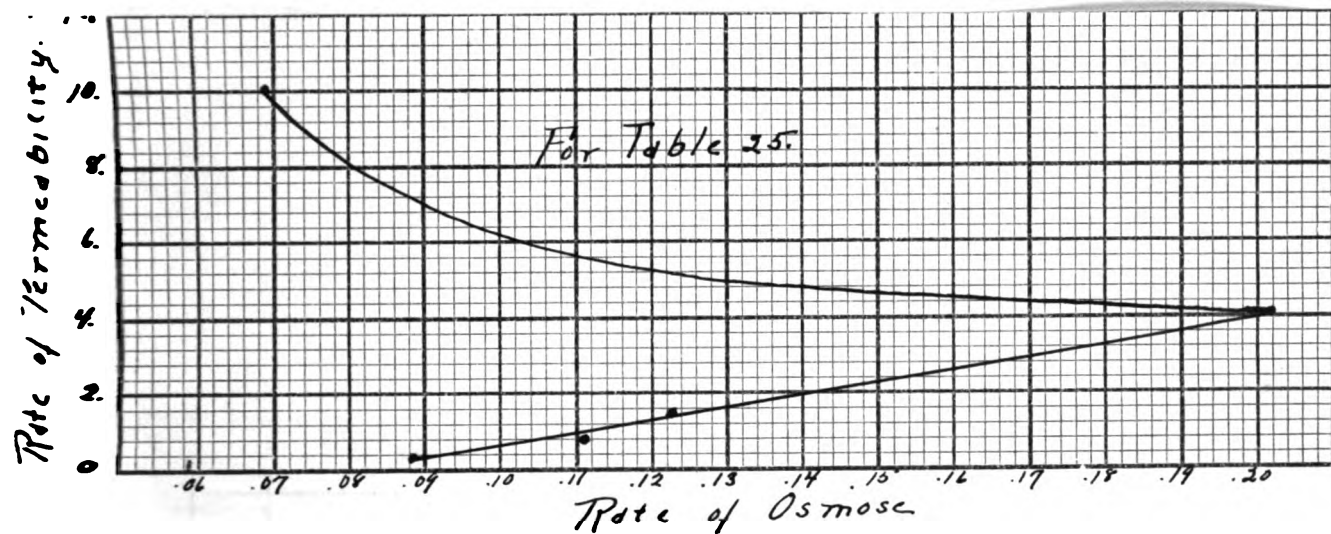
Rate of Osmose

The accompanying tables show in each case the solution and membrane used, the size and weight of the membrane, and the rate of endosmose and permeability expressed in cm/sec. As the voltage is a factor, it is also given along with the temperature. The current, size of the bubble, and direction of flow are also added. In addition in the later tables the rate of endosmose is calculated to cm/sec per volt.

The first trial, represented by Table 9 and its accompanying curve, was made on asbestos membranes built up in the manner previously discussed. These were kept under water until ready for use. The asbestos was not weighed but simply built up of varying thicknesses. The permeability was measured by attaching a suction pump to one end of the apparatus, with the bubble tube removed, and sucking water through the membrane under a vacuum of 1/2 inch. This was found to be unsatisfactory, so the subsequent permeability measurements were made by the method previously described. There was not much regularity in the curve.

The second set, Table 10 and its curve, was made up by using 6 gms of dry asbestos in each case and varying the pressure to secure the difference in permeability. The asbestos used had been thoroughly washed and dried before weighing, and washed again after building up the membrane; but the curve was still irregular. Table 11 is merely a repetition of Table 10, after the membrane had been in pure water for a day. The general nature of the curve was the same except for an increase in endosmose rate in each case. This suggested that perhaps the time of contact with water might have a measurable effect so in the next

tables are listed the periods of contact _with water._ In the next set, Table 12,
the same weight and pressure was used in each case and the curve
has the same general shape as before. Further, there was no
duplication; a matter to be discussed later.

Asbestos, proving unsatisfactory, a soft porcelain
battery cup was ground up and meshed. That portion passing a
40 but not a 50 mesh sieve was washed and made into the membranes
used in the next run, Table 13. These were made using the same
weight and varying the pressure. It was found that they tended
to disintegrate during the flow, the porcelain being too soft.
To overcome this difficulty, a much harder grade of porcelain
was obtained and Table 14 represents the results with 100 mesh,
varying the weight with the same pressure. Duplication was also
tried here _but_ unsuccessfully. These membranes remained quite com-
pact but the glass wool plugs became a dark brown due to the
migration of the binder used in making the original plate. It
was then washed with hot water, dried, meshed again and built up
into membranes giving the results in Table 15. Doubtless a large
error due to the solubility of the membrane was introduced here
and because of such lack of regularity it was decided to try
filter paper.

The paper used was the best obtainable: Schleicher and
Schüll, acid washed of varying grades and Whatman's No. 40. These
papers were cut in circles of the desired size and then placed in
water, or the solution to be used, for at least twelve hours
before measuring. The use of such gave the possibility of varying
the thickness of the membrane at will and of duplicating not

evident in the previous work. One difficulty which presented itself was that of the removal of air bubbles. This was first attempted by applying suction to both electrode tubes, after filling, but this almost invariably ruptured the membrane. It was found satisfactory to merely soak and shake, and then press firmly together before placing in the apparatus.

The first runs using paper were still not very regular as shown by Table 16, and its curve, but it was during this set that the apparatus was broken, and the new one had larger electrode tubes which altered the sensitiveness. However, Table 17, using S & S paper No. 590--Table 18, using S & S paper Np. 589--Table 19, using S & S paper No. 595--Table 20, using Whatman's No. 40, and Table 21 using ordinary qualitative paper, all gave the same type of curve when the rate of endosmose was plotted against the rate of permeability.

Because it was so apparent that permeability was a factor affecting electric endosmose, the rate of permeability was determined for all runs with non aqueous solutions. Not only was this done with the pure solvent in the same series of gradation as with water, but this factor was measured for each membrane used, to note if it might not explain some of the other peculiarities. S & S paper No. 589 was chosen in each case as the most satisfactory.

Table 22 and its curve is for acetone, Table 23 for amyl alcohol, Table 24 for nitrobenzene, Table 25 for pryridine, Table 26 for benzaldehyde, and Table 27 for n-butyl alcohol. It will be noted that the effect is the same whether the endosmose

is + (toward the cathode) or - (toward the anode). It will also
be noted that the curve is much steeper above than below the
maximum showing that a change of permeability up to the maximum
has a much smaller effect upon the endosmose rate than beyond.
Further, the maximum does not appear at the same number of thick-
nesses for different membranes or different solvents. This deter-
mination was made at the very beginning of a set of runs with a
particular solvent, thus serving as a means of selecting the most
rapid membrane. A possible explanation of this phenomenon will
be suggested in the final discussion.

ADSORPTION EXPERIMENTS

Because so much of the theoretical discussion suggested
that adsorption was the greatest factor in determining electric
endosmose some simple effects were tried. Filter papers were
soaked first in a medium having a highly adsorbable ion like H
and one with a low adsorbing factor like Cl. This membrane was
then taken out, washed and placed in the apparatus which was
filled with pure water., The rate was greatly reduced, but not
reversed. Other substances of like nature gave similar results.
Upon using Na NO_3, where the anion is most highly adsorbed, the
rate was greatly increased. Similar substances also gave like
results. In water solution, as has been shown by many investiga-
tions, adsorption is a predominating factor. Just how effective
it is in non aqueous solvents will be considered later.

EXPERIMENTS WITH NON AQUEOUS SOLVENTS

Some of this work (continuous runs and permeability effect) has already been discussed and will not be repeated.

PREPARATION OF SOLVENTS AND SOLUTES

The water used in these experiments was distilled from $K MnO_4$ and had a very low conductivity as shown by amperage readings under high voltage.

The acetone was Baker's analyzed, Lot 61019 Sp. Gr. 0. 799. It was dried by standing over anhydrous $Cu SO_4$ and fractionated between 56° and 56.8°. It was necessary in most cases to recover some of the solvent for use in later experiments and this was first distilled from the dissolved salts and then treated in the same manner as for the previous purification.

The amyl alcohol used was Baker's analyzed, Lot 63718, Sp. Gr. 0. 805. This was dried in a similar manner and fractionated at 129.8°--130.6°. Because this solvent seemed unique, in that it gave negative endosmose and thinking this might be due to occluded acetic acid, it was distilled from lime and then treated as before.

The nitrobenzene was Merck's highest purity. Some difficulties were also experienced in the first runs with this solvent, thought at the time to be due to an impurity, but later found to be caused by cleaning acid not being thoroughly removed. However, it was treated with Na_2CO_3, dried, and fractionated at 206.0° to 207.5°. No attempt was made to remove any dinitrobenzene which might be present.

The pyridine--Merck's quality, was fractionated after long standing over highest purity KOH. It had a boiling point of 114.0° to 115.0°.

The benzaldehyde was Merck's highest purity and no attempt was made to further purify, on account of oxidation effects. It had a boiling point of 178.3° to 179.2°.

The n-butyl alcohol was Eastman's research product No. 50, and boiled at 116.8°-117.5°. Although this also gave negative endosmose, only a small quantity was distilled from lime and dried, giving the same result.

The salts used were either Merck's or Baker's highest purity and were merely dried and kept in closed weighing bottles in a desiccator. In one or two cases it was impossible to obtain the pure product and these were recrystallized and then dried. Calculations for the preparation of solutions were made on the dry basis.

DUPLICATION

No successful attempts have previously been made to duplicate results obtained in electric endosmose through a duplication of membranes. In fact, former workers on membranes have found this one of their greatest problems.[92] Instead of making such attempts, the membrane which had been cut from a plate or built up in the manner described was merely washed out and used again. When we realize the difficulty involved in removing occluded substances

92. Bartell and Co-workers. Loc. cit.

we see how important this is. Particularly is this true in the
case of water where the electrolysis of the substance itself
produces highly adsorbed ions. Furthermore, most substances
are, to a greater or less extent, soluble in water and even a
very slight solubility might produce a highly adsorbed ion which
would have an appreciable effect upon the rate of flow. Just
how difficult this duplication with water and an asbestos mem-
brane was is shown in Table 12. With porcelain and water Table
14 gives the results. Even when the porcelain was washed, dried,
remeshed and washed again with hot water, the results did not
duplicate (Table 28). In fact, it was seen in Tables 10 and 11
that a second run on the same membrane after soaking and washing
did not give the same results.

TABLE 28

February 10, '20.

Porcelain (100 mesh) vs. Water.

Membrane No.	Weight	Vacuum used	Voltage	Current	Direction	Temp.	Bubble	Time of Soaking	cm/sec Osmose	cm/sec Permeability
15 gm.	15 in.	128.0	2-6	+	25°	5 m.m.	17 hrs.	0.177	2.96
"	"	"	3-6	+	"	3 " "	12 "	0.089	3.05
"	"	"	2-3	+	"	4 " "	22.5"	0.126	3.60
"	"	"	2	+	"	5 " "	24.5"	0.093	3.36

TABLE 29

Asbestos vs. H_2O.

Date	Weight	Vacuum used	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec Permeability
an. 9	6 gm.	15 in.	127.0	4	+	25°	5.5 m.m.	0.196	1.08
an.12	" "	" "	127.0	2	+	"	6 " "	0.196	1.23
an.13	" "	" "	117.0	1-2	+	"	_____	0.258	----
an.27	" "	" "	128.0	8	+	"	.7 " "	0.450	1.63
eb. 11	" "	" "	127.5	2-3	+	"	3 " "	0.203	1.59

TABLE 30

March 17, '20.

Filter Paper vs H₂O.

No.of Run No.	Thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
10		S. & S. No. 597	125.0	2-3	+	25°	4.5 m.m.	0.074	51 x 10⁻⁵	0.82
	8	"	125.0	2-3	+	"	3 " "		0.052	48 x "	0.91
	8	"	122.0	2-3	+	"	3 " "		0.048	39 x "	0.98
	8	"	125.0	2-3	+	"	5 " "		0.063	50 x "	1.01
	8	"	123.0	2-2.5	+	"	5 " "		0.050	41 x "	1.06

TABLE 31

March 20, '20.

Filter Paper vs. H₂O.

Run No.	No.of Thickness	Kind	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
1	8	S. & S. No.589	125.0	1	+	25°	5 m.m.	0.060	48 x 10⁻⁵	1.20
2	"	"	125.0	1	+	"	2.5 "	0.067	54 x "	1.21
3	"	"	125.0	1	+	"	4 " "	0.075	60 x "	1.30
4	"	"	118.0	1	+	"	5 " "	0.065	55 x "	1.27
5	"	"	118.5	1	+	"	6 " "	0.096	81 x "	1.10
6	"	"	118.0	1	+	"	4 " "	0.060	51 x "	0.97
7	"	"	124.0	1	+	"	5 " "	0.110	89 x "	0.74
8	"	"	123.0	1	+	"	5 " "	0.063	51 x "	1.09

TABLE 32

May 10, '20.

Filter Paper vs. H_2O.

No.of Thick-ness	Kind	Voltage	Current	Direc-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
8	S & S No.597	393.0	5.0	+	25^0	7 m.m.	0.417	10.6×10^{-4}	0.66
"	"	"	4.0	+	"	5 " "	0.338	8.6 x "	0.84
"	"	"	5.0	+	"	3 " "	0.350	8.9 x "	0.58
"	"	"	5.0	+	"	6 " "	0.297	7.5 x "	0.43
"	"	"	5.0	+	"	4.5" "	0.483	12.2 x "	1.08
"	"	"	5.0	+	"	5 " "	0.341	8.6 x "	1.11

TABLE 33

March 26, '20.

Filter Paper vs. H_2O.

No.of Thick-ness	Kind	Voltage	Current	Direc-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
8	S & S No. 589	122.5	1	+	25^0	5 m.m.	0.070	57×10^{-5}	0.78
"	"	122.5	1	+	"	4 " "	0.049	40 x "	0.84
"	"	116.0	1	+	"	5 " "	0.049	42 x "	0.77
"	"	122.0	1-2	+	"	4 " "	0.107	88 x "	0.63
"	"	122.0	1-1.5	+	"	5 " "	0.082	69 x "	0.67
"	"	122.0	1-1.5	+	"	5 " "	0.077	63 x "	0.46
"	"	122.0	1	+	"	4 " "	0.055	45 x "	0.47
"	"	120.0	1-1.5	+	"	3 " "	0.092	77 x "	0.31

TABLE 34

April 6, '20.

Acetone vs. Filter Paper.

No. m.	No.of Thick-ness	Kind	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
-A	8	3 & 5 No.589	642.5	0	+	25°	6 m.m.	2.970	44.8 x 10^{-4}
-A	"	"	"	0	+	"	7 " "	2.608	40.5 x "
-A	"	"	"	0	+	"	8 " "	2.438	37.9 x "
-A	"	"	"	0	+	"	8 " "	2.343	36.4 x "
-A	"	"	"	0	+	"	9 " "	2.222	34.5 x "
-A	"	"	406.5	0	+	"	9 " "	0.983	24.1 x "
-A	"	"	"	0	+	"	9 " "	0.943	23.1 x "
-A	"	"	"	0	+	"	9 " "	1.081	26.5 x "
-A	"	"	642.5	0	+	"	9 " "	2.230	33.1 x "
-B	"	"	"	0	+	"	3 " "	4.016	62.5 x "
-B	"	"	"	0	+	"	3.5" "	3.365	52.3 x "
-B	"	"	"	0	+	"	5.0" "	3.092	48.1 x "
-B	"	"	406.5	0	+	"	5.5" "	1.485	36.5 x "
-B	"	"	"	0	+	"	5.5" "	1.403	34.5 x "

TABLE 35

April 7, '20.

Acetone vs Filter Paper.

No. of un Thick-ness	Kind	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
·A 8	S & S No.589	642.5	0+	+	25°	5 m.m.	3.083	47.9 x 10^{-4}
·A "	"	642.5	0+	+	"	5 " "	2.521	39.2 x "
·A "	"	406.5	0	+	"	6 " "	1.181	29.2 x "
·B "	"	642.5	0+	+	"	4 " "	5.555	86.4 x "
·B "	"	642.5	0+	+	"	6 " "	4.304	66.9 x "
·B "	"	406.5	0	+	"	8 " "	2.059	50.7 x "
·B "	"	642.5	0+	·+	"	7 " "	4.296	66.8 x "
·B "	"	406.5	0	+	"	9 " "	2.059	50.7 x "

TABLE 36

April 8, '20.

Acetone vs. Filter Paper.

No. of un Thick-ness	Kind	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
·A 8	S & S No.589	642.5	0+	+	25°	7 m.m.	4.296	66.8 x 15^{-4}	
·B "	"	406.5	0	+	"	9 " "	2.059	50.7 x "	1.10
·A "	"	642.5	0	+	"	8 " "	4.261	66.3 x "	
·B "	"	406.5	0	+	"	9 " "	2.125	52.2 x "	2.80
·A "	"	642.5	0	+	"	3 " "	4.296	66.8 x "	
·B "	"	406.5	0	+	"	4 " "	2.180	53.6 x "	2.00
·A "	"	642.5	0	+	"	4 " "	4.198	65.3 x "	
·B "	"	406.5	0	+	"	5 " "	2.081	51.1 x "	1.70
·A "	"	642.5	0	+	"	4 " "	4.316	69.0 x "	
·B "	"	406.5	0	+	"	5 " "	2.166	53.2 x "	2.60

TABLE 35

April 7, '20.

Acetone vs Filter Paper.

No. of Thick-ness		Kind	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
-A	8	S & S No.589	642.5	0+	+	25°	5 m.m.	3.083	47.9×10^{-4}
-A	"	"	642.5	0+	+	"	5 " "	2.521	39.2 x "
-A	"	"	406.5	0	+	"	6 " "	1.181	29.2 x "
-B	"	"	642.5	0+	+	"	4 " "	5.555	86.4 x "
-B	"	"	642.5	0+	+	"	6 " "	4.304	66.9 x "
-B	"	"	406.5	0	+	"	8 " "	2.059	50.7 x "
-B	"	"	642.5	0+	+	"	7 " "	4.296	66.8 x "
-B	"	"	406.5	0	+	"	9 " "	2.059	50.7 x "

TABLE 36

April 8, '20.

Acetone vs. Filter Paper.

Run No.	No. of Thick-ness		Kind	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
1-A	8		S & S No.589	642.5	0+	+	25°	7 m.m.	4.296	66.8×15^{-4}	
1-B	"		"	406.5	0	+	"	9 " "	2.059	50.7 x "	1.10
2-A	"		"	642.5	0	+	"	8 " "	4.261	66.3 x "	
2-B	"		"	406.5	0	+	"	9 " "	2.125	52.2 x "	2.80
3-A	"		"	642.5	0	+	"	3 " "	4.296	66.8 x "	
3-B	"		"	406.5	0	+	"	4 " "	2.180	53.6 x "	2.00
4-A	"		"	642.5	0	+	"	4 " "	4.198	65.3 x "	
4-B	"		"	406.5	0	+	"	5 " "	2.081	51.1 x "	1.70
5-A	"		"	642.5	0	+	"	4 " "	4.316	69.0 x "	
5-B	"		"	406.5	0	+	"	5 " "	2.166	53.2 x "	2.60

TABLE 37   69

May 13, '20.

Amyl Alcohol vs. Filter Paper.

Run No.	Mem- brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
	6 Thick- ness	Amyl Alco-								
1	S&S-589	hol	623.0	0	-	25°	7.5 m.m.	0.158	2.5×10^{-4}	0.24
2	"	"	"	0	-	"	7 " "	0.133	$2.1 \times$ "	0.22
3	"	"	"	0	-	"	7.5 " "	0.138	$2.2 \times$ "	0.23
4	"	"	"	0	-	"	5.5 " "	0.197	$3.1 \times$ "	0.22
5	"	"	"	0	-	"	4 " " "	0.156	$2.5 \times$ "	0.26

TABLE 38

May 31, '20.

Nitro Benzene vs. Filter Paper.

Run No.	Mem- brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
	8 Thick- ness	Nitro Ben-								
1	S&S-589	zene	555.0	0	+	25°	6 m.m.	0.725	13.0×10^{-4}	0.68
2	"	"	"	0	+	"	3.5" "	0.965	$17.3 \times$ "	0.88
3	"	"	"	0	+	"	3 " "	0.741	$13.3 \times$ "	0.85
4	"	"	"	0	+	"	3 " "	0.855	$15.4 \times$ "	0.98

TABLE 39

June 12, '20.

Pyridine vs. Filter Paper.

Run No.	Mem- brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
	6 Thick- ness	Pyri- dine								
1	S&S-589	"	841.0	0+	+	26.5^o	4.5 m.m.	0.124	18.8×15^{-5}	1.57
2	"	"	"	0+	+	"	3.5 " "	0.083	$9.8 \times$ "	1.50
3	"	"	"	0+	+	"	3.5 " "	0.082	$9.7 \times$ "	1.87
4	"	"	"	0+	+	"	5.5 " "	0.083	$9.8 \times$ "	1.66

TABLE 40

June 21, '20.

Benzaldehyde vs. Filter Paper.

m Mem- b. brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
8 Thick- ness 848-589	Bens- alde- hyde "	954.0	0.5	+	25°	4.0 m.m.	0.290	30.3 x 10⁻⁵	0.94
"	"	"	0.5	+	"	4.5 " "	0.897	31.0 x "	0.90
"	"	"	0.5	+	"	4.5 " "	0.299	31.3 x "	0.92
"	"	"	0.5	+	"	3.0 " "	0.207	21.6 x "	0.84

TABLE 41

July 2, '20.

N-Butyl Alcohol vs Filter Paper.

m Mem- b. brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
6 Thick- ness 848-589	N- Butyl Alco- hol	940.0	1.0	-	26°	5 m.m.	0.188	19.7 x 15⁻⁵	0.67
"	"	"	1.0	-	"	6 " "	0.189	19.7 x "	0.50
"	"	"	1.0	-	"	5 " "	0.191	20.0 x "	0.54
"	"	"	1.0	-	"	7.5" "	0.188	19.7 x "	0.57
"	"	"	1.0	-	"	4.5" "	0.176	18.4 x "	0.54

In one case the same membrane--known as membrane No.3-
Set No. 2, Asbestos--was kept for several weeks, washed thoroughly
and run on several occasions and the results were far from being
the same. (Table 29).

Even with filter paper when using water, the duplication
of endosmose was very poor (Tables 30, 31 and 32). Table 32 repre-
sents runs on papers which had been washed with two daily changes
for a period of two months, before running. In one case, Table 33,
a number of runs were made on the same membrane with a determina-
tion of permeability and a thorough washing after each run. In
most cases this difference cannot be attributed to a difference
in permeability, as where the endosmose was the same the permea-
bility rate often varied, and vice versa.

But this seems to be a difficulty only in the case of
water, and as all previous work was with this solvent it is an
extremely important one. Non aqueous solutions in most cases
duplicated very well. The papers were merely soaked in the
medium under consideration and taken out when needed, using a
new membrane for each run. This also made it possible to ac-
quire a large mass of data in a comparatively short time.

Table 34 represents runs on acetone using throughout
the same membrane: 8 thicknesses of S & S paper No. 589. In
some cases the duplication was good and in others poor. Table
35, using different membranes and solutions through a shorter
series of runs gives better results. Note here the voltage
also fluctuated some. Just how accurately it is possible to check

results is shown in Table 36 where the membrane and solution were renewed for each pair of runs.

Duplication with amyl alcohol is shown in Table 37. This is not quite so good. With nitrobenzene (Table 38), pyridine (Table 39), benzaldehyde (Table 40), and n-butyl alcohol (Table 41), such runs were also made.

Properties of the solvent might have some effect upon such runs. For example: the substances most difficult to duplicate had the highest viscosity. Further, water is a unique substance in many respects; its high dielectric constant giving it a dissociating and dissolving power not manifested by the others. Also a slight impurity might for this reason have a larger effect. Both pyridine and benzaldehyde had some action upon the brass connectors, an argument in favor of short runs. Benzaldehyde is also oxidized readily in the air producing a relatively strong acid. On the whole, the errors are less apparent when the membrane and solution are changed for each short run.

THE EFFECT OF VARYING THE APPLIED POTENTIAL.

Earlier work on electric endosmose indicated that the endosmose was a linear function of the applied voltage. As with other related phenomena this had only been tried out with water and found to hold except at high voltages - (500 volts).[93] Acetone was first tried and it is interesting to note that the cur-

93. Briggs. Loc. cit.

rent was very low, only 1 milliampere, even when applying a
voltage of 1011 volts. Table 42 and its curve show the results
using the same membrane throughout the run. The curve is not a
straight line. It will be noted that the run was made by start-
ing at a low voltage and gradually increasing to the maximum.
To test this further, another trial was made, starting at the
maximum and going down, with the results shown in Table 43.
This curve was even further removed from a straight line except
up to about 800 volts. To test if this discrepancy was due to
the use of a single membrane, another run, Table 44, was made,
changing the membrane and solution for each change of voltage.
This curve is also not a straight line. In the curves the
voltage is plotted against the rate of endosmose.

TABLE 42

April 5, '20.

ACETONE

Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
Thickness 348-589	Acetone "	58.5	0	+	25^0	4 m.m.	0.129	22×10^{-4}
"	"	116.0	0	+	"	4 " "	0.295	25 x "
"	"	175.0	0	+	"	5 " "	0.473	27 x "
"	"	282.5	0	+	"	6 " "	0.613	26 x "
"	"	290.5	0	+	"	6.5" "	0.735	25 x "
"	"	348.5	0	+	"	7 " "	0.761	21 x "
"	"	406.5	0	+	"	7 " "	0.852	20 x "
"	"	465.5	0	+	"	7 " "	0.874	18 x "
"	"	524.5	0	+	"	7 " "	0.964	18 x "
"	"	583.5	0	+	"	7 " "	1.023	17 x "
"	"	642.5	0	+	"	7 " "	1.056	16 x "
"	"	701.5	0	+	"	7 " "	1.167	16 x "
"	"	760.5	0	+	"	7 " "	1.190	15 x "
"	"	819.5	1-	+	"	7 " "	1.339	16 x "
"	"	878.5	1-	+	"	7 " "	1.369	15 x "
"	"	937.5	1-	+	"	7 " "	1.587	15 x "
"	"	1011.5	1	+	"	7 " "	1.863	18 x "
"	"	44.0	0	+	"	6 " "	0.052	11.8 x "
"	"	29.5	0	+	"	6 " "	0.037	12.4 x "

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TABLE 48

April 15, '20.

ACETONE.

Mem- brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
8 Thick- ness	Ace- tone							
S&S-589	"	994.0	0	+	25°	4 m.m.	4.545	45.7 x 10⁻⁴
"	"	921.0	0	+	"	4 " "	2.979	32.3 x "
"	"	863.0	0	+	"	5 " "	1.972	22.8 x "
"	"	806.0	0	+	"	6.5" "	1.334	16.5 x "
"	"	748.0	0	+	"	7 " "	1.163	15.5 x "
"	"	690.0	0	+	"	7.5" "	1.009	14.6 x "
"	"	633.0	0	+	"	7.5" "	0.883	13.9 x "
"	"	576.0	0	+	"	8 " "	0.772	13.4 x "
"	"	519.0	0	+	"	8.5" "	0.656	12.6 x "
"	"	461.0	0	+	"	8.5" "	0.542	11.7 x "
"	"	404.0	0	+	"	8.5" "	0.458	10.8 x "
"	"	347.0	0	+	"	8.5" "	0.562	10.4 x "
"	"	289.0	0	+	"	8.5" "	0.281	9.7 x "
"	"	231.0	0	+	"	8.5" "	0.218	9.4 x "
"	"	173.0	0	+	"	8.5" "	0.155	8.9 x "
"	"	115.0	0	+	"	8.5" "	0.099	8.6 x "
"	"	58.0	0	+	"	8.5" "	0.051	8.7 x "

TABLE 44

April 19, '20.

ACETONE

a Mem- brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
8 Thick- ness	Ace- tone								
848-589	"	994.0	1-	↗	25^0	6 m.m.	5.000	50.3×10^{-4}	0.85
"	"	863.0	1-	←	"	5 " "	2.744	31.7 x "	0.69
"	"	748.0	0+	←	"	6 " "	2.394	31.9 x "	1.45
"	"	633.0	0	←	"	5 " "	2.000	31.5 x "	0.88
"	"	519.0	0	←	"	6 " "	1.529	27.5 x "	1.17
"	"	404.0	0	←	"	5 " "	0.689	17.0 x "	1.47
"	"	289.0	0	←	"	5 " "	0.466	16.1 x "	0.92
"	"	173.0	0	←	"	6 " "	0.344	19.8 x "	0.95

TABLE 45

May 7, '20.

WATER

m.	Mem-brane	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
8	Thick-ness S&S-589	H_2O "	111.0	1.5	+	25^0	5.5m.m.	0.049	4.4×10^{-4}
	"	"	167.0	2-3	+	"	"	0.061	3.5 x "
	"	"	223.0	4	+	"	"	0.078	3.5 x "
	"	"	279.0	5-6	+	"	"	0.128	4.5 x "
	"	"	335.0	7	+	"	"	0.239	7.1 x "
	"	"	393.0	8	+	"	"	0.402	10.1 x "
	"	"	451.0	11	+	"	"	0.531	11.7 x "
	"	"	508.0	12	+	"	"	0.686	13.5 x "
	"	"	566.0	14	+	"	"	0.823	14.5 x "
	"	"	623.0	17	+	"	"	0.958	15.3 x "
	"	"	679.0	18	+	"	"	1.222	17.9 x "
	"	"	736.0	20	+	"	"	1.274	17.3 x "
	"	"	793.9	22	+	"	"	1.406	17.7 x "

TABLE 46

May 11, '20.

Amyl Alcohol

a Mem- brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	om/sec Osmose	om/sec/volt Osmose
8 Thickness 3&3-589	Amyl Alcohol	978.0	0+	-	25^0	4.5m.m.	0.277	2.8×10^{-4}
"	"	906.0	0	-	"	"	0.260	2.8 x "
"	"	793.0	0	-	"	"	0.216	2.7 x "
"	"	679.0	0	-	"	"	0.175	2.5 x "
"	"	566.0	0	-	"	"	0.140	2.4 x "
"	"	451.0	0	-	"	"	0.109	2.1 x "
"	"	336.0	0	-	"	"	0.078	2.3 x "
"	"	223.0	0	-	"	"	0.051	2.2 x "
"	"	111.0	0	-	"	"	0.025	2.2 x "

TABLE 47

May 29, '20.

Nitrobenzene   Permeability = 0.88 cm/sec

Mem-brane	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
6 Thick-ness 343-589	Nitro-ben-zene	971.0	O	+	25°	4.5m.m.	1.461	15.0×10^{-4}
"	"	898.0	O	+	"	"	1.168	13.0 x "
"	"	785.0	O	+	"	"	0.817	10.4 x "
"	"	669.0	O	+	"	"	0.562	8.4 x "
"	"	555.0	O	+	"	"	0.391	7.0 x "
"	"	441.0	O	+	"	"	0.259	5.8 x "
"	"	329.0	O	+	"	"	0.156	4.7 x "
"	"	218.0	O	+	"	"	0.081	3.7 x "
"	"	109.0	O	+	"	"	0.035	3.1 x "

TABLE 48

June 10, '20.

Pyridine

Permeability = 0.83 cm/sec

m Mem-). brane	Solu- tion	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
8 Thick- ness SAS-589	Pyri- dine "	971.0	1.0	+.	27.0^{0}	4 m.m.	0.082	8.4×10^{-5}
"	"	898.0	0.5+	+	"	"	0.071	7.9 x "
"	"	785.0	0.5	+	"	"	0.060	7.6 x "
"	"	669.0	0.5-	+	"	"	0.049	7.3 x "
"	"	555.0	0	+	"	"	0.043	7.7 x "
"	"	441.0	0	+.	"	"	0.037	8.3 x "
"	"	329.0	0	+	"	"	0.030	8.8 x "
"	"	218.0	0	+	"	"	0.023	10.4 x "
"	"	109.0	0	+	"	"	0.012	11.0 x "

TABLE 49

June 21, '20.

Benzaldehyde

Permeability = 1.15 cm/sec.

m No.	Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
6	Thick-ness S&3-589	Benz-alde-hyde	954.0	0.5	+	25°	5m.m.	0.121	12.6 x 10^{-5}
	"	"	883.0	0.5	+	"	"	0.110	12.3 x "
	"	"	772.0	0	+	"	"	0.096	12.4 x "
	"	"	659.0	0	+	"	"	0.080	12.1 x "
	"	"	549.0	0	+	"	"	0.064	11.6 x "
	"	"	437.0	0	+	"	"	0.050	11.4 x "
	"	"	326.0	0	+	"	"	0.038	11.3 x "
	"	"	216.0	0	+	"	"	0.024	11.1 x "
	"	"	107.0	0	-+	"	"	0.011	10.2 x "

TABLE 50

July 3, '20.

n-Butyl Alcohol   Permeability = 0.67 cm/sec

n.	Mem-brane	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
6	Thick-ness 8&8-589	n-Butyl Alco-hol	954.0	1.0	-	26°	5.5m.m.	0.188	19.7×10^{-4}
	"	"	883.0	1.0	-	"	"	0.171	19.3 x "
	"	"	772.0	1.0	-	"	"	0.147	19.0 x "
	"	"	659.0	0.5	-	"	"	0.126	19.1 x "
	"	"	549.0	0.5	-	"	"	0.104	18.9 x "
	"	"	437.0	0	-	"	"	0.083	18.9 x "
	"	"	326.0	0	-	"	"	0.062	19.0 x "
	"	"	216.0	0	-	"	"	0.042	19.4 x "
	"	"	107.0	0	-	"	"	0.021	19.6 x "

For Table 42.

Rate of Osmose

For Table 43.

Rate of Osmose

For Table 44

Rate of Osmose

For Table 45

Rate of Osmose

For Table 46.

Rate of Osmose

For Table 47.

Rate of Osmose

For Table 48.

Rate of Osmose

For Table 49.

Voltage.

Rate of Osmose

For Table 50.

Rate of Osmose
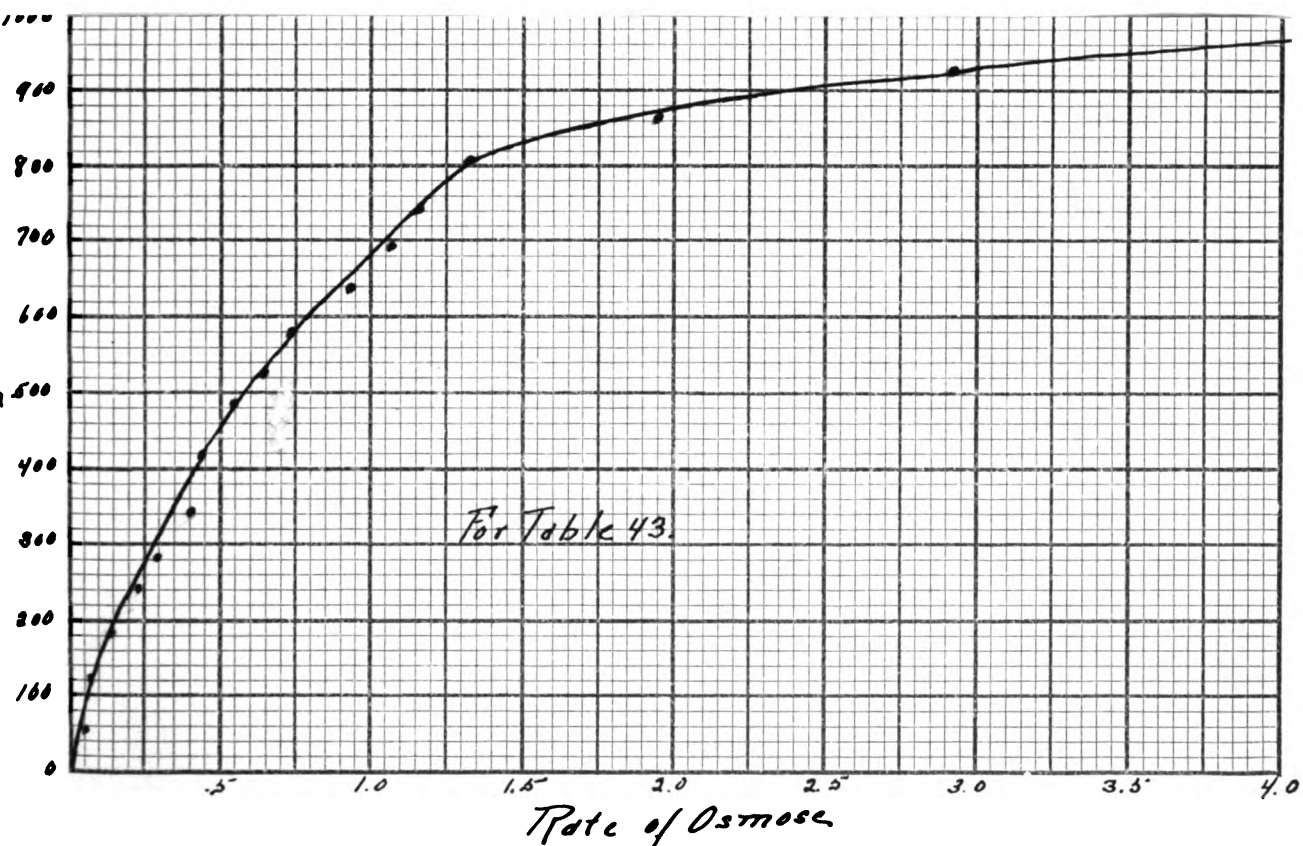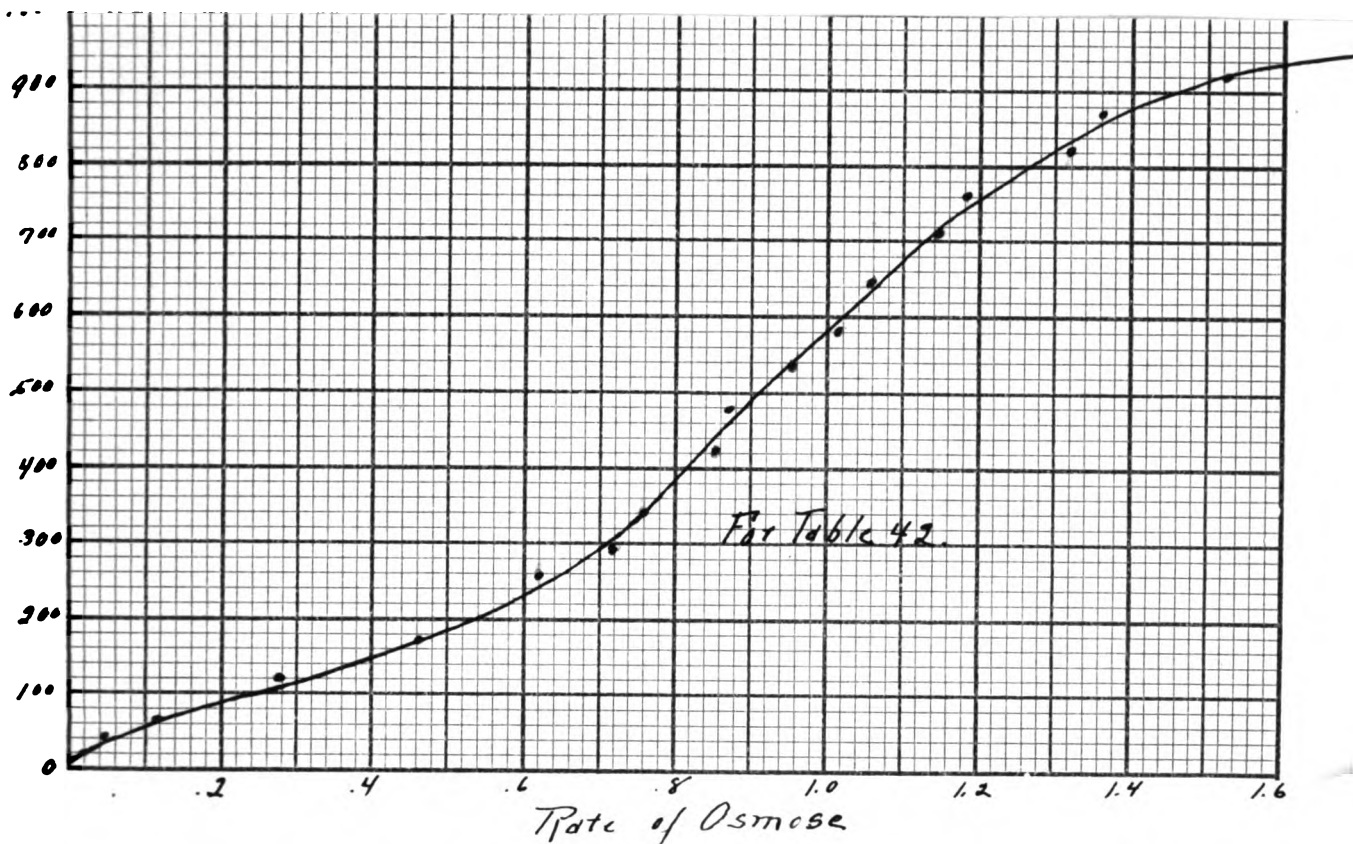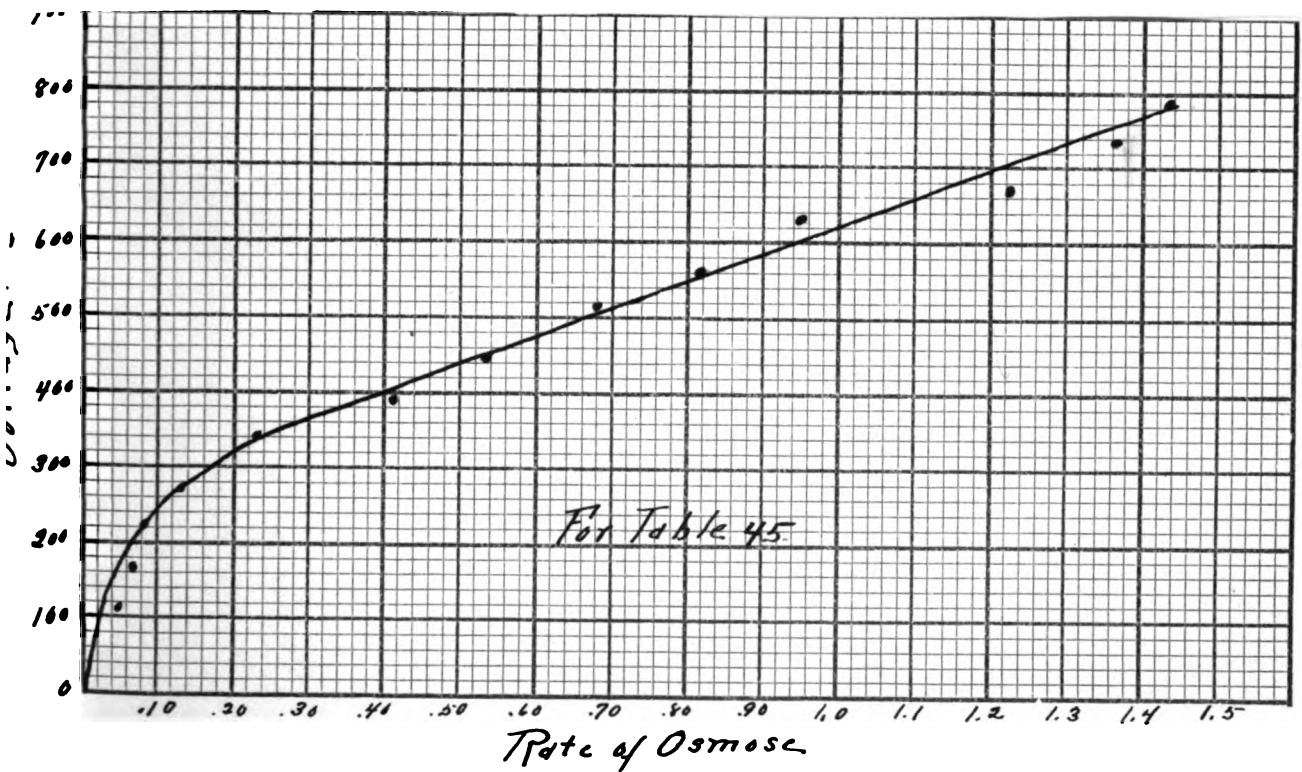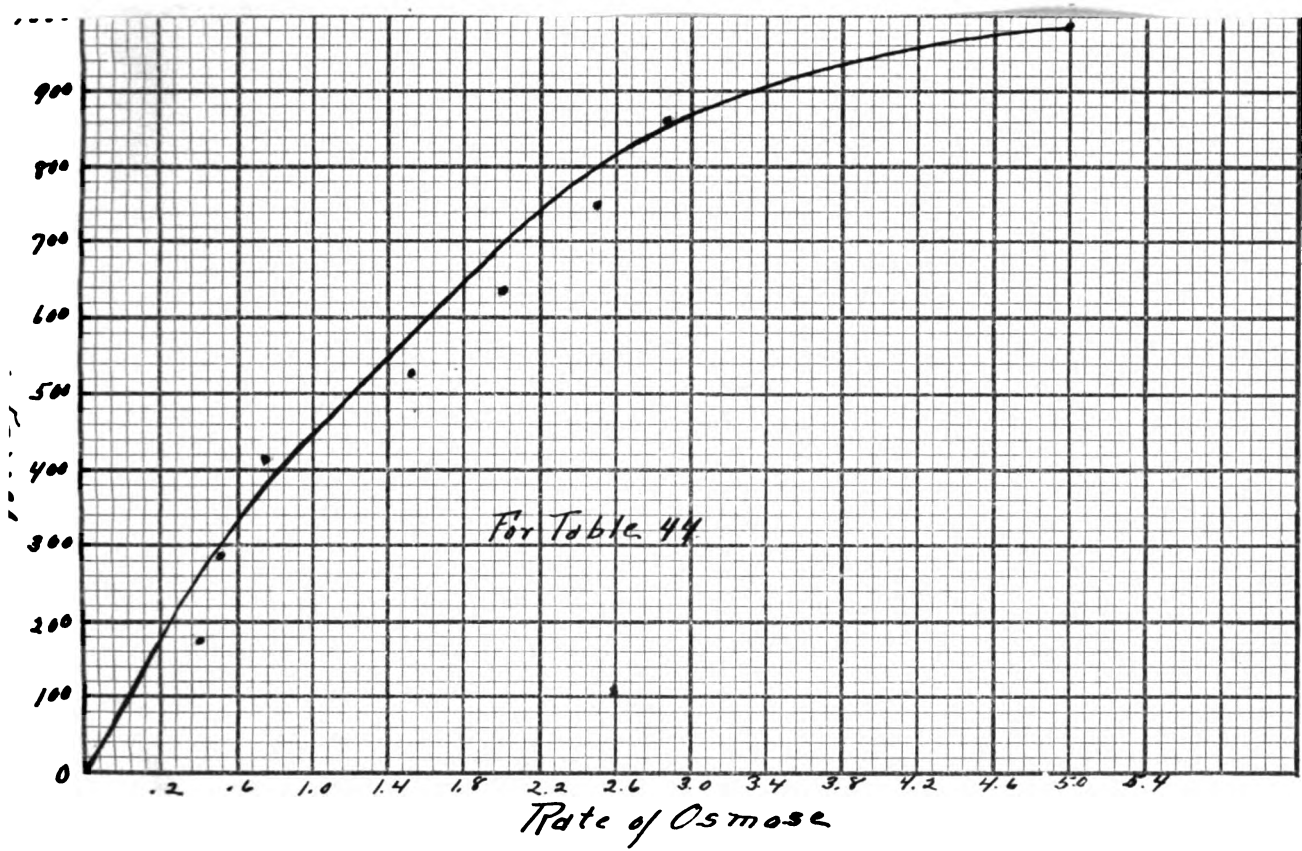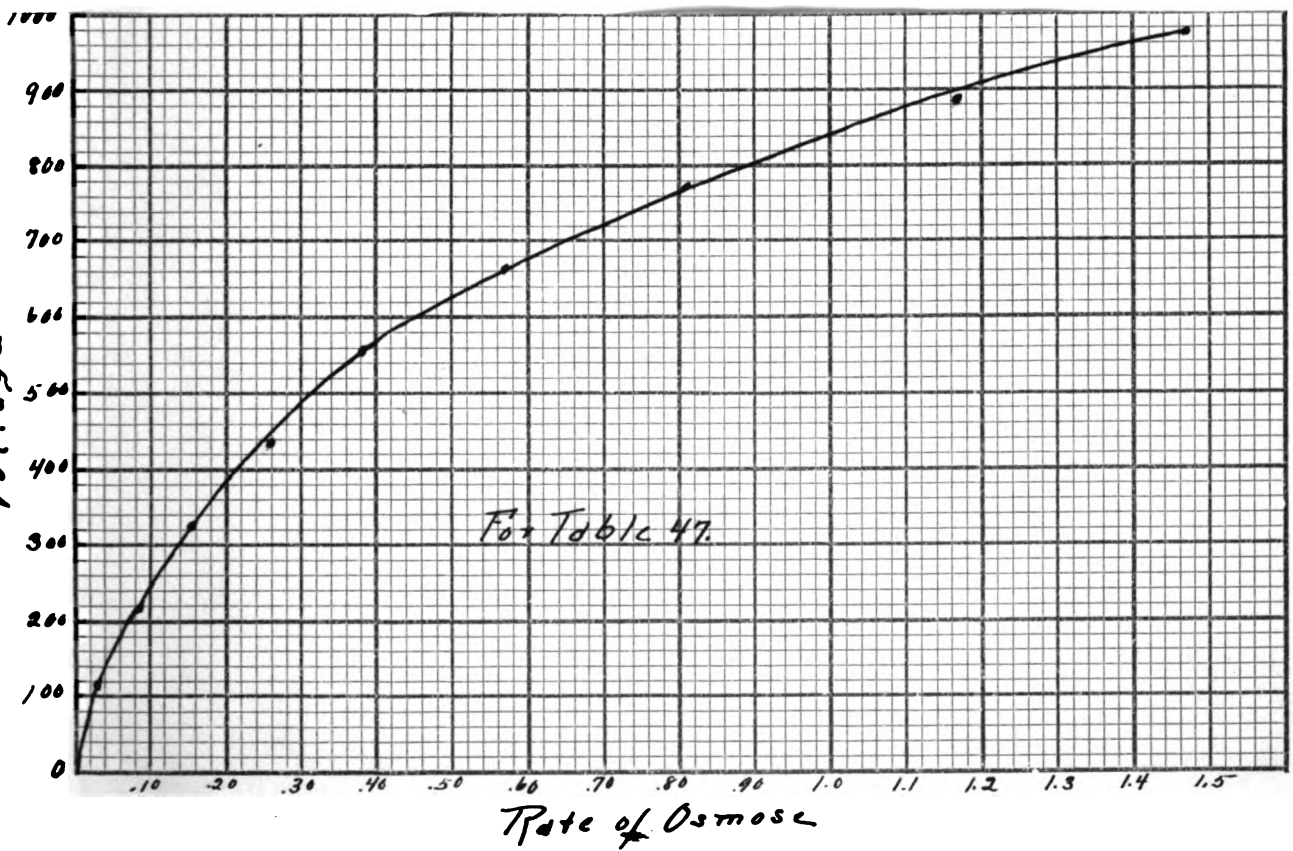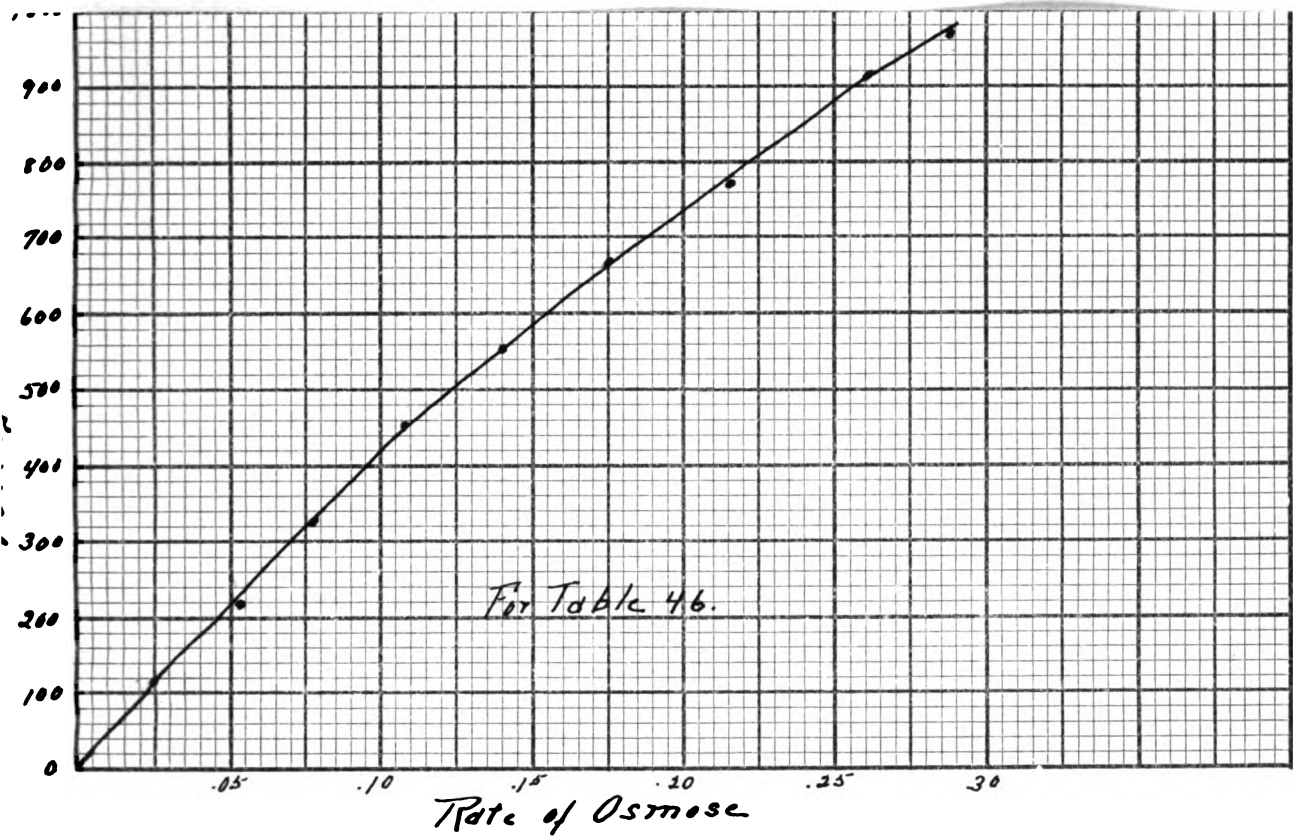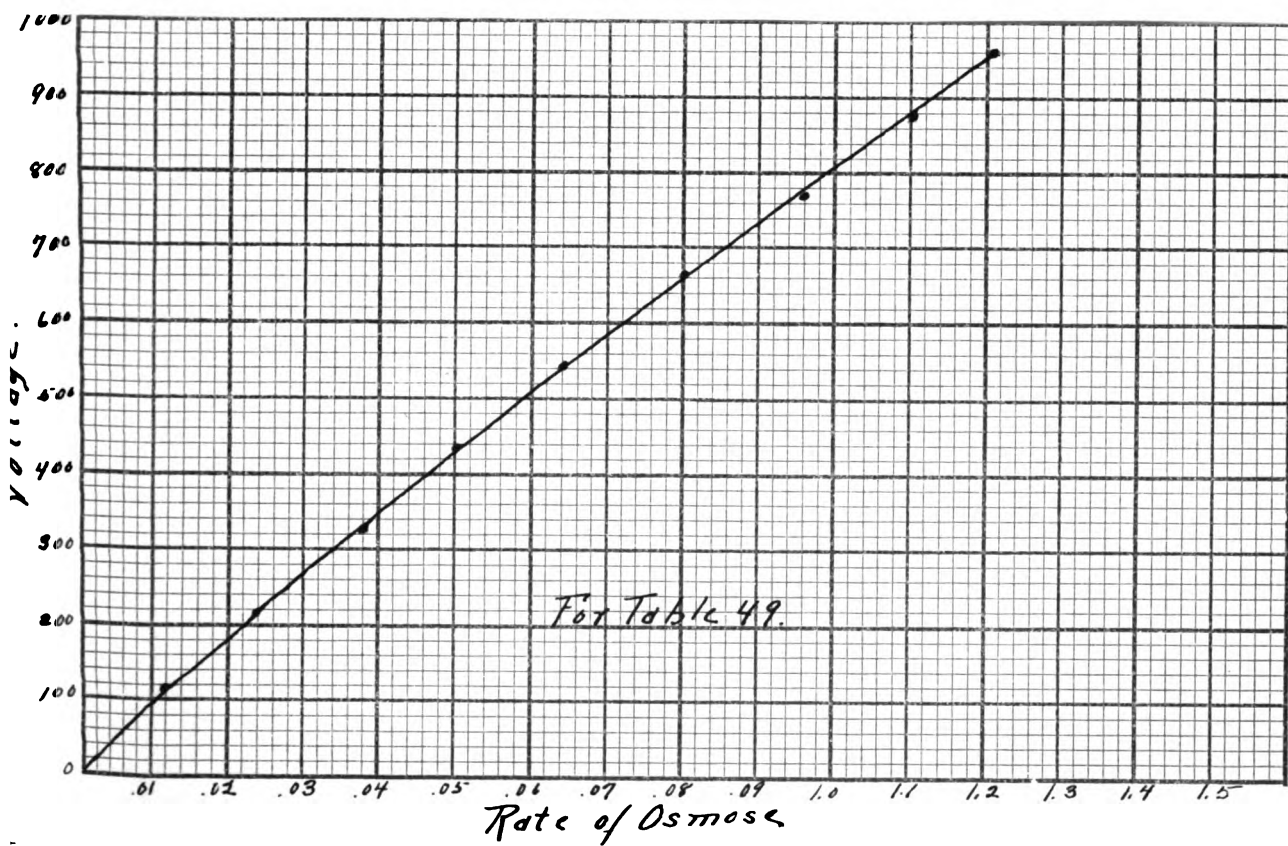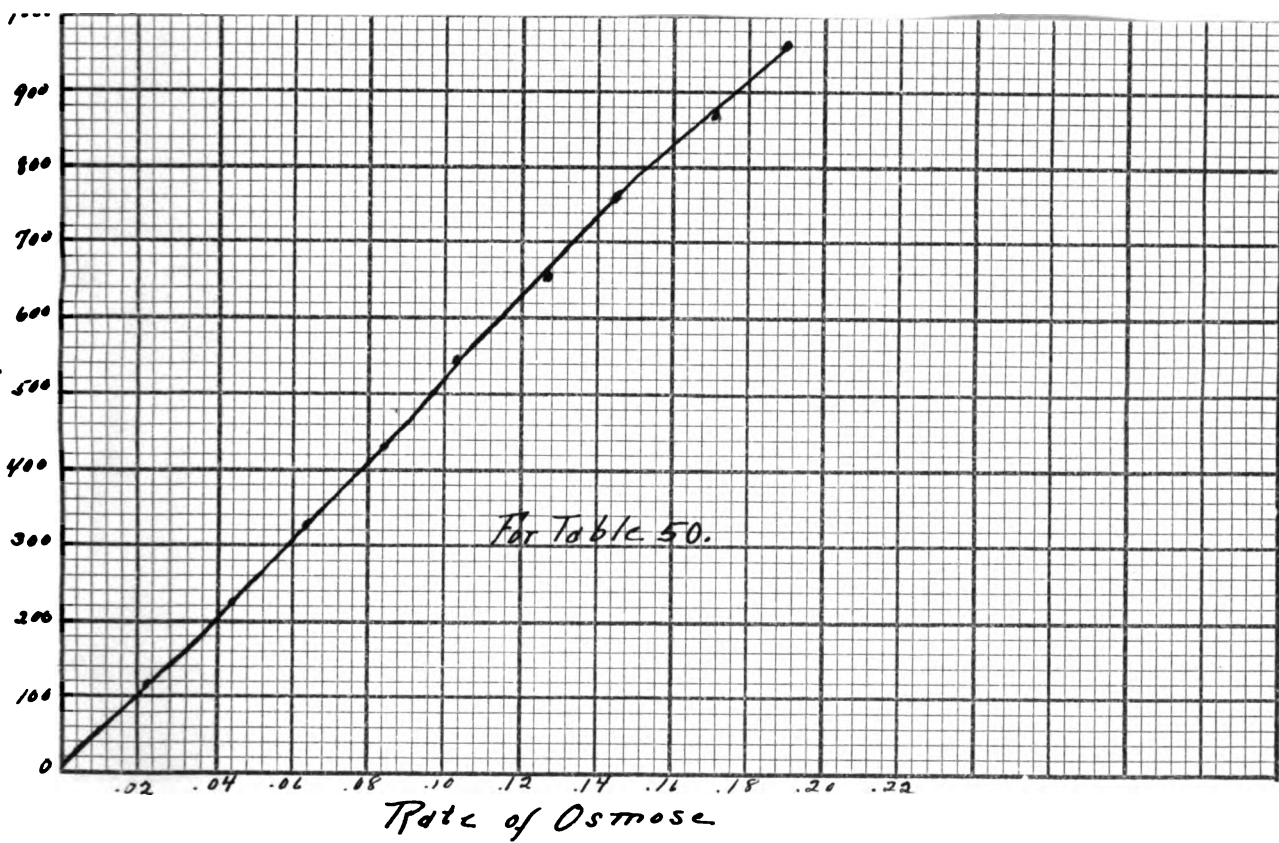
This was also tried with water, Table 45, giving a
curve irregular at high voltages. Such a curve was also obtained
with amyl alcohol, Table 46; nitrobenzene, Table 47; pyridine,
Table 48; benzaldehyde, Table 49; and n-butyl alcohol, Table 50.
In each of the cases the run was made in a very short time
using the same membrane throughout. The curves for amyl al-
cohol, benzaldehyde and n-butyl alcohol approximate nearly
straight lines, but in general there is a too rapid increase of
endosmose with the applied voltage. But both amyl alcohol and
nitrobenzene exhibited at high voltage a tendency to pile up
in the electrode tubes, or chamber into which the solution was
flowing, due to the fact that the high viscosity did not per-
mit it to flow out into the measuring tube as fast as it came
through the membrane. A voltage at which this effect was not
apparent was used for subsequent runs. This effect, if cor-
rected, would throw the higher points of the curve farther to
the right, thus shifting the whole farther from a straight
line. Most of the non aqueous solvents were noted to be quite
frictionless against the glass, in fact, pyridine and benzal-
dehyde were almost entirely so. This was a great advantage as
dirt and grease caused little error. The only disturbing fac-
tor was that of viscosity. Further, very high voltages could
be studied without electrolysis effects as will be seen by
noting the very low current readings given in milliamperes.
Amyl alcohol and nitrobenzene gave absolutely no current
reading with the highest voltage obtainable and the maximum

in any case was 1 milliampere, It should be noted again that both amyl and n-butyl alcohols gave negative endosmose, while the others were positive.

It appears that the rate of endosmose is not a linear function of the voltage above a certain maximum, but is more or less materially increased with a corresponding shifting of the points to the right.

THE EFFECT OF THE ADDITION OF ACID AND ALKALI

Work with water solutions has in most cases shown a reversal of flow in acid solution when the original membrane was negatively charged, due to the adsorption of the H ion present. The OH ion of the base tends to increase the flow through a negative membrane and decrease or even reverse the flow through a positive membrane. Though this is generally true also in the consideration of non aqueous solvents, variations are noted doubtless due to chemical action between the acid or alkali and the solvent. Also cellulose was one of the substances found by Perrin[94] to give no acid reversal.

The acid selected for these runs was succinic, because of its high solubility in most organic solvents and the ease with which it could be obtained in a pure dry condition and weighed. The alkali used was NaOH, Merck's highest purity. In weighing, every precaution was used to keep it as free from moisture as possible. The solutions were made up of a concentration of N/100 and then diluted to N/1000, N/10000, N/100000 and N/1000000. The least concentrated was always run first to prevent errors due to insufficient rinsing of the apparatus.

94. Loc. cit.

The results with acetone are shown in Table 51 and
its accompanying curve. The curves are plotted with the con-
centration of acid and alkali, increasing from the neutral in
each case, against the rate of endosmose. There is here an
increase from the neutral with increasing concentration of both
acid and alkali. With the acid there should be a decrease due
to the adsorption of the H ion tending to neutralize the nega-
tive contact charge of the membrane which is directing and deter-
mining the endosmotic flow. To test if this was a feature of the
succinic acid alone some acetone was charged with dry HCl gas.
The results were similar.

TABLE 51

April 16, '20.

ACETONE

Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
8 Thickness 848-889	N/1000 Succinic	289.0	1 -	+	25°	6m.m.	4.109	145.6X10^{-4}	0.55
"	N/500 "	"	1.0	+	"	4" "	3.373	116.6X "	1.77
"	N/100 " (Neu-)	"	1.5	+	"	4" "	4.297	148.6X "	0.60
"	(tral)	"	0	¥	"	5" "	1.267	43.7X "	1.25
"	N/1000 NaOH	"	0	+	"	5" "	2.081	72.0X "	1.31
"	N/500 "	"	0	+	"	4" "	2.105	72.5X "	1.14
"	N/100 "	"	1.0	+	"	4" "	5.016	173.5X "	1.31

TABLE 52

May 15, '20.

Amyl Alcohol

a Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
6 Thick-Succinic ness									
S&S-589	N/100000	623.0	0	-	25°	8 m.m.	0.097	1.5 x 10⁻⁴	0.32
"	N/10000	"	0	-	"	4 " "	0.102	1.6 x "	0.27
"	N/1000	"	0	-	"	5 " "	0.078	1.2 x "	0.24
"	N/100	"	0	-	"	4 " "	0.077	1.2 x "	0.28
"	Neutral NaOH	"	0	-	"	7.5" "	0.158	2.5 x "	0.24
"	N/100000	"	0	-	"	7.5" "	0.041	0.6 x "	0.22
"	N/10000	"	0	+	"	8 " "	0.063	1.0 x "	0.26
"	N/1000	"	1.5	+	"	4 " "	0.080	1.2 x "	0.26
"	N/100	"	2.5	+	"	8 " "	0.045	0.7 x "	0.25

TABLE 53

June 1, '20.

Nitrobenzene

Membrane & Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
	Succinic								
S&S-589	N/100000 "	555.0	0	+	25°	3.5m.m.	1.013	18.2×10^{-4}	0.85
"	N/10000 "	"	0	+	"	5.5" "	0.979	17.6 x "	0.80
"	N/1000 "	"	0	+	"	4 " "	0.572	10.3 x "	0.75
"	N/100 "	"	0	+	"	4.5" "	0.304	5.4 x "	0.68
"	Neutral NaOH	"	0	+	"	6 " "	0.725	13.0 x "	0.68
"	N/100000	"	0	+	"	4 " "	0.612	11.0 x "	0.68
"	N/10000 "	"	0	+	"	3 " "	0.664	11.9 x "	0.66
"	N/1000 "	"	0	+	"	4 " "	1.158	20.8 x "	0.50
"	N/100 "	"	0	+	"	4 " "	1.055	15.0 x "	0.55

TABLE 54

June 14, '20.

PYRIDINE

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
	Succinic								
S&S-589	N/100000	841.0	0.5	+	26.5°	6 m.m.	0.141	16.7×10^{-5}	1.62
"	N/10000	"	1.0	+	"	5.5" "	0.177	21.0 x "	1.50
"	N/1000	"	1.0	+	"	6 " "	0.130	15.4 x "	1.57
"	N/100	"	1.5	+	"	4 " "	0.037	4.3 x "	1.57
"	Neutral NaOH	"	0	+	"	3.5" "	0.083	9.8 x "	1.50
"	N/100000	"	0	+	"	4 " "	0.093	11.0 x "	1.50
"	N/10000 "	"	0	+	"	5 " "	0.098	11.6 x "	1.51
"	N/1000 "	"	0.5	+	"	5 " "	0.275	32.6 x "	1.42
"	N/100 "	"	1.5	+	"	4 " "	0.973	115.7 x "	1.66

TABLE 55

June 22, '20.

BENZALDEHYDE

n Mem-brane	Solution	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
8 Thick-ness	Succinic								
548-569	N/100000 "	954.0	0.5	+	25°	6 m.m.	0.129	13.5×10^{-5}	0.88
"	N/10000 "	"	0.5	+	"	4.5" "	0.285	29.8 x "	0.87
"	N/1000 "	"	0.5+	+	"	6.5" "	0.179	18.7 x "	0.85
"	N/100 "	" "	1.0-	↕	"	4 " "	0.414	43.3 x "	0.85
"	Neutral NaOH	"	0.5	↕	"	4.5" "	0.297	31.0 x "	0.90
"	N/100000 "	"	1.0	+	"	7 " "	0.380	39.8 x "	0.85
"	N/10000 "	"	1.0	+	"	6 " "	0.346	36.2 x "	0.86
"	N/1000 "	"	1.0+	+	"	5 " "	0.403	42.2 x "	0.90
"	N/100 "	"	1.5	+	"	4.5" "	0.243	25.4 x "	0.85

TABLE 56

July 5, '20.

n-Butyl Alcohol

m Mem-brane	Solution	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
6 Thick-ness									
SAS-589	Succinic N/100000 "	954.0	1.0	-	26°	6 m.m.	0.134	14.0 x 10^{-5}	0.47
"	N/10000 "	"	1.0	-	"	5 " "	0.116	12.4 x "	0.55
"	N/1000 "	"	1.0	-	"	5 " "	0.107	11.2 x "	0.52
"	N/100 "	"	1.0	-	"	5 " "	0.103	10.7 x "	0.52
"	Neutral NaOH "	"	1.0	-	"	5 " "	0.188	19.7 x "	0.67
"	N/100000 "	"	1.0	-	"	4 " "	0.128	13.4 x "	0.54
"	N/10000 "	"	1.5	-	"	4 " "	0.219	22.9 x "	0.50
"	N/1000 "	"	5.0	+	"	4 " "	0.076	7.9 x "	0.52
"	N/100 "	"	21.5	+	"	4 " "	0.239	25.0 x "	0.51

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For Table 51.

Rate of Osmose

For Table 52.

To Cathode ←   → To anode

Rate of Osmose

For Table 53

Rate of Osmose.

For Table 54.

Rate of Osmose.

$\frac{N}{100000}$

$\frac{N}{10000}$

$\frac{N}{1000}$

$\frac{N}{100}$

.05   .10   .15   .20   .25   .30   .35

For Table 55.

Rate of Osmose.

.12 .14 .16 .18 .20 .22 .24 .26 .28 .30 .32 .34 .36 .38 .40

For Table 56.

To Cathode ←   → To Anode

.24 .26 .16 .12 .08 .04   0   .04 .08 .12 .16 .20 .24
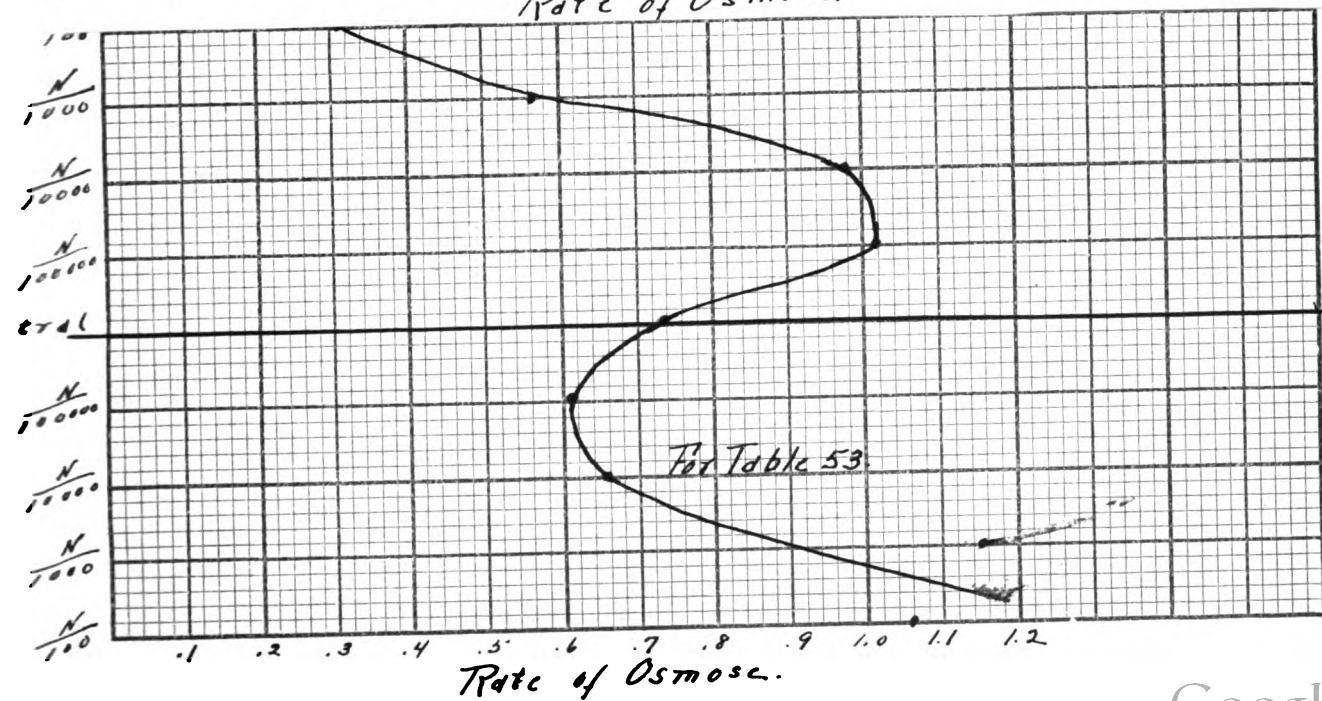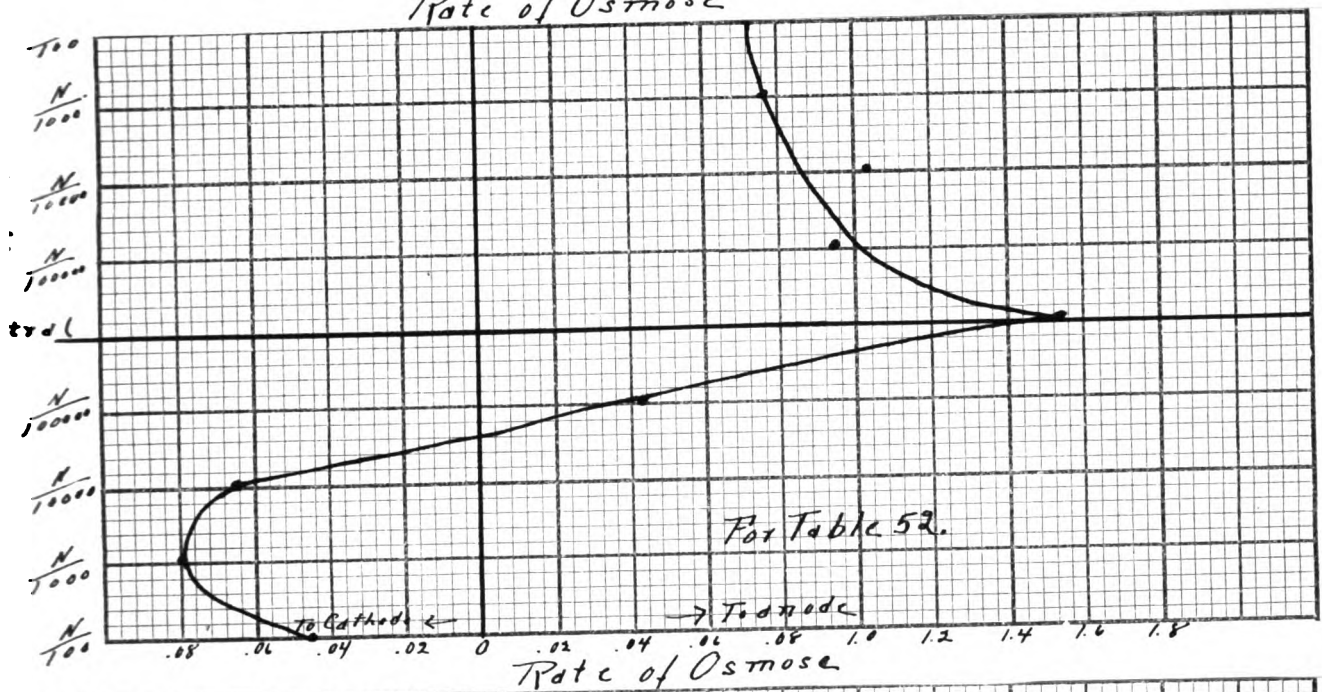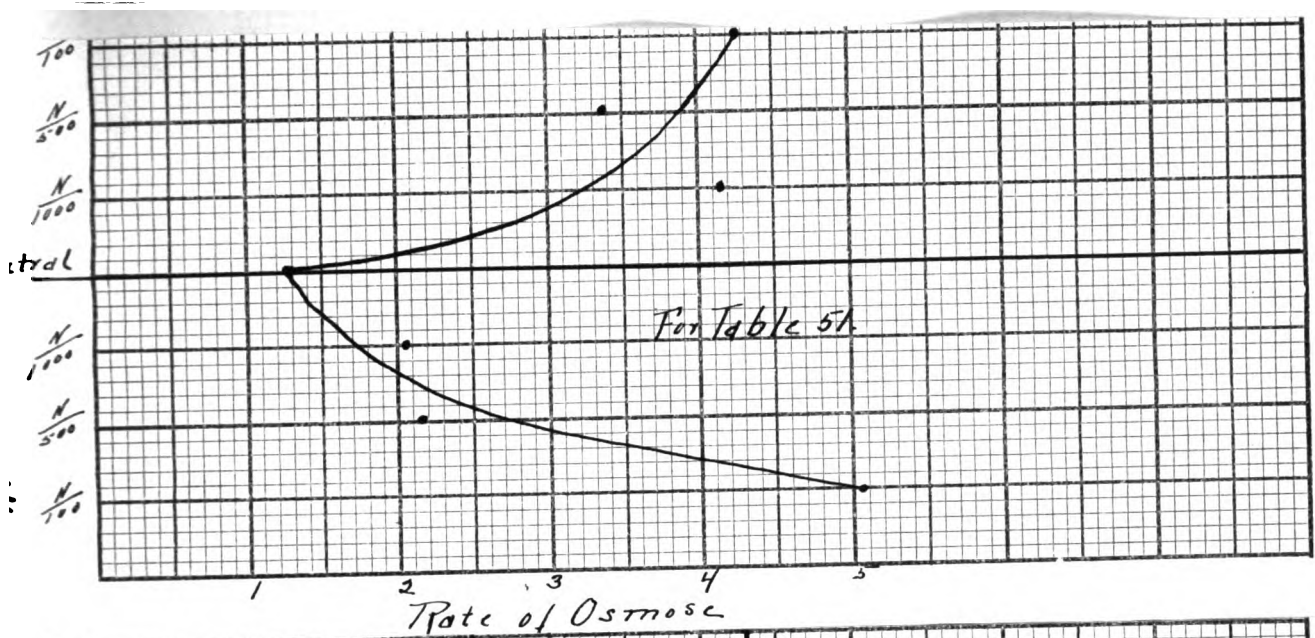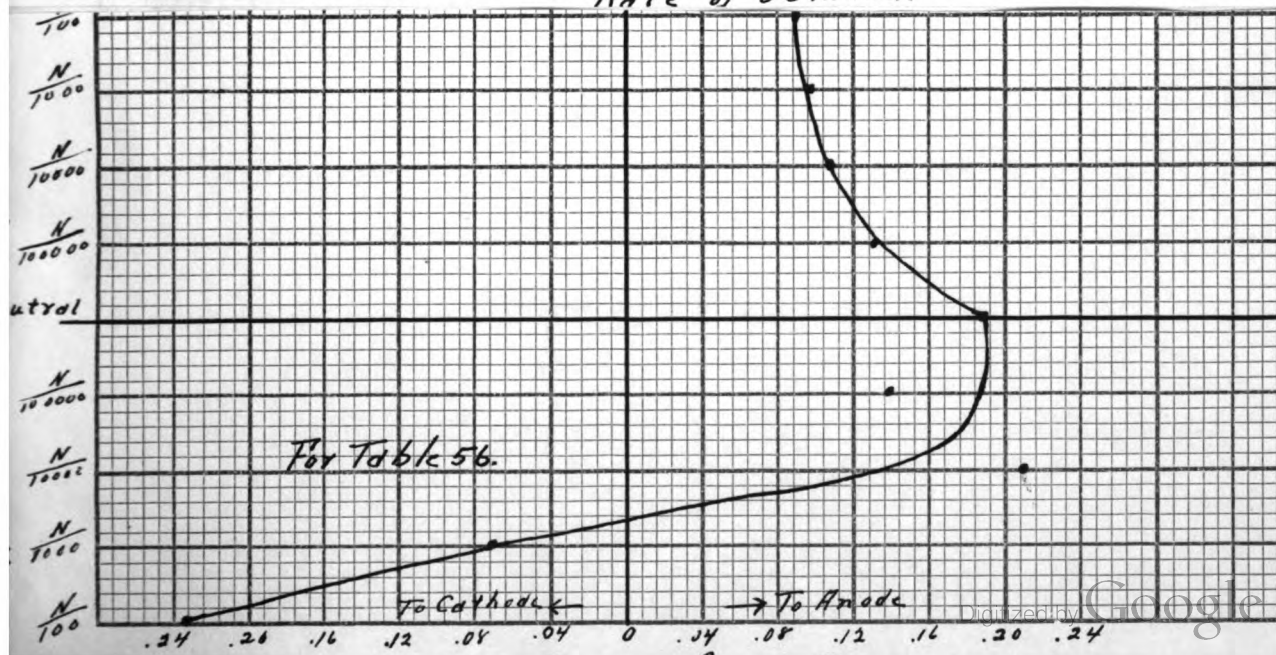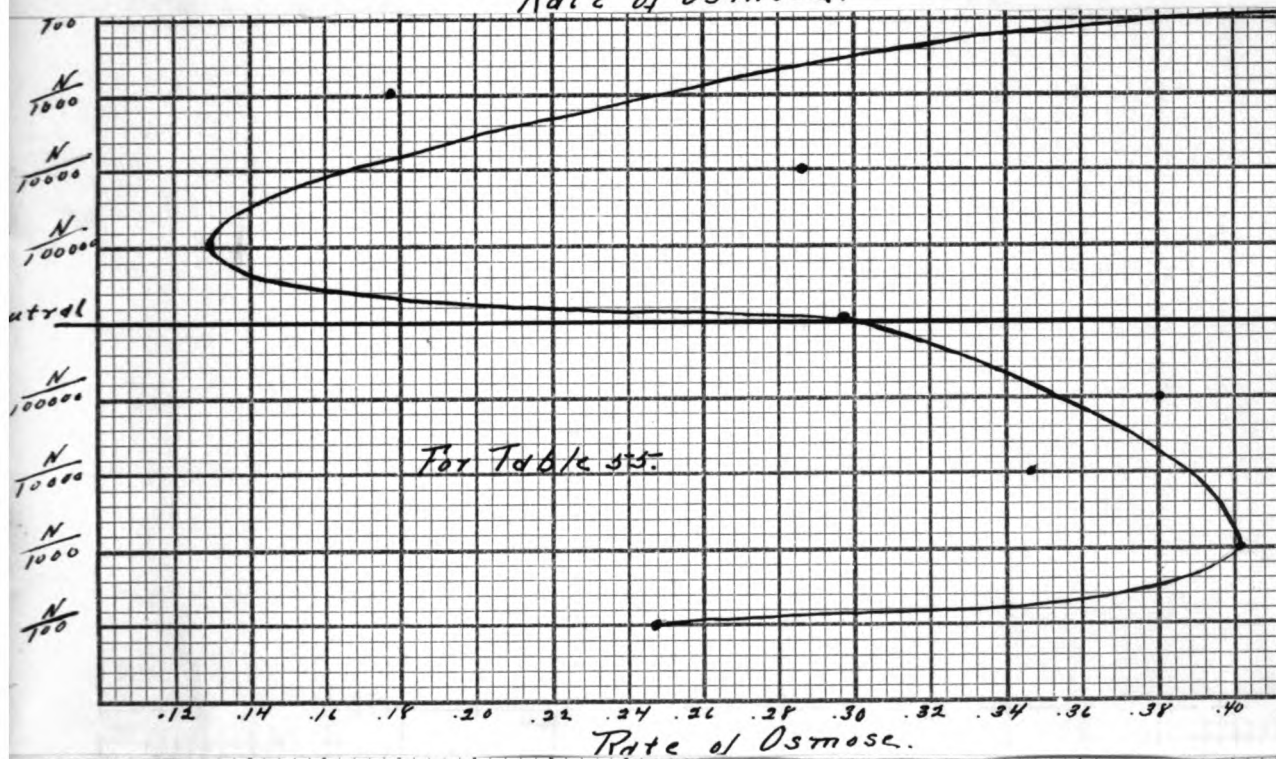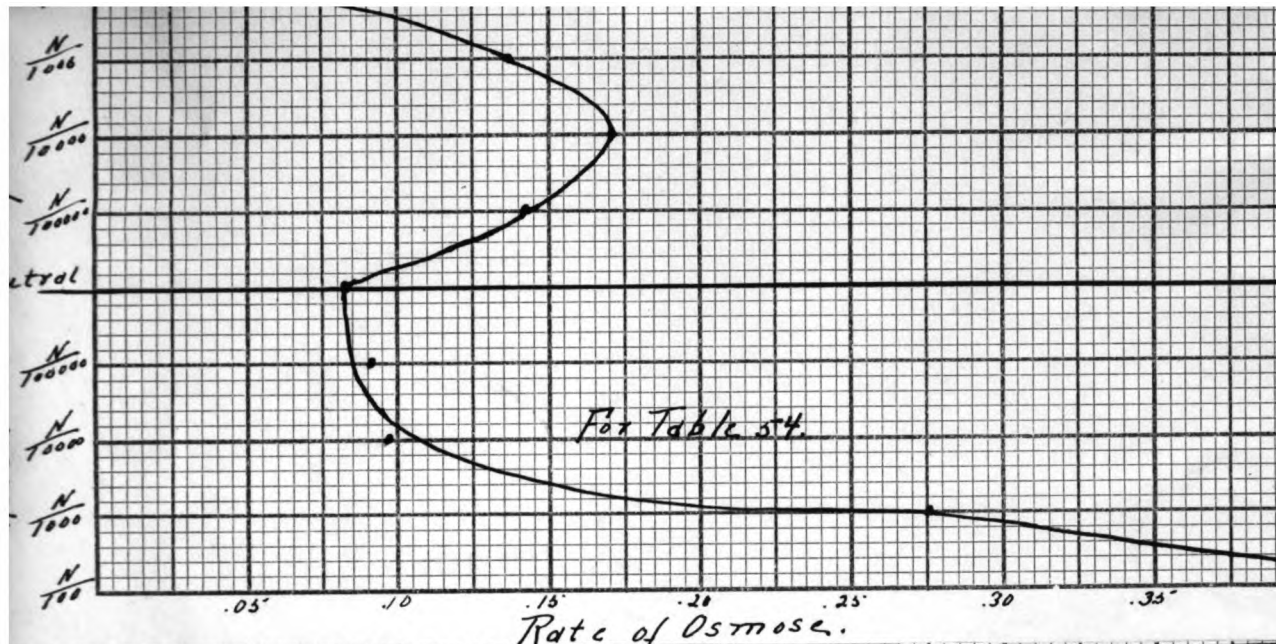
The amyl alcohol curve (Table 52), is perfectly regular in regard to the alkali which with increasing concentration tends by adsorption of the OH ion, first, to decrease to zero and then increase to a maximum. This decrease again at higher concentration is important and will be noted again in the study of concentration effects. The acid curve decreases slightly with increasing concentration toward the anode when, unless its maximum is very low, it should increase.

Table 53 shows the nitrobenzene curve. In this both acid and alkali show a maximum. The acid rate falls off from this point with increasing concentration while that of the alkali increases. Here the Na OH was difficultly soluble and some particles were left in the N/100 solution. The pyridine curve (Table 54), is almost a counterpart of this. Benzaldehyde, however, (Table 55), is quite irregular and was in large part due to chemical action with the solute and oxidation in the air. There is no question in this case about the action of NaOH on the solvent and furthermore it did not all dissolve but left many particles in the more concentrated solution.

The n-butyl alcohol curve, Table 56, is almost the same as that for amyl alcohol, as might be expected from its chemical nature and similarity in other runs.

EFFECT OF TEMPERATURE CHANGE

It has been noted in a previous section that the coefficient of viscosity of the liquid medium enters the accepted equation for electric endosmose in the denominator. As the viscosity

varies with the temperature this factor was varied to find the effect on the rate of flow. Briggs[95] found in the case of water that the curve of endosmose against temperature was not a straight line and suggested an equation for temperature correction.

A temperature run was made upon each solvent studied. In the bath, either cooled with ice or warmed by adding hot water, was placed the apparatus filled with the pure solvent, and after equilibrium was attained, other factors being kept constant, there were obtained the results illustrated in the accompanying tables and curves. The temperature is plotted against rate of endosmose.

95. Loc. cit.

TABLE 57

April 14, '20.

ACETONE

n Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
S&S-589	Acetone	406.5	0	+	20.9^0	3 m.m.	1.556	38.2×10^{-4}
"	"	"	0	+	24.8^0	3 " "	1.605	$39.4 \times$ "
"	"	"	0	+	27.5^0	7 " "	1.588	$39.0 \times$ "
"	"	"	0	+	30.0^0	7 " "	1.315	$32.3 \times$ "
"	"	"	0	+	33.0^0	8 " "	1.090	$26.8 \times$ "

TABLE 58

April 29, '20.

ACETONE

n Membrane Thickness	Solution Acetone	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S&S-589	"	289.0	0+	+	22.0^0	5 m.m.	0.600	20.7×10^{-4}	0.88
"	"	"	0+	+	20.1^0	8 " "	0.645	$22.3 \times$ "	0.98
"	"	"	0+	+	35.5^0	8-12 " "	0.630	$21.7 \times$ "	0.86
"	"	"	0+	+	40.2^0	8-15 " "	0.474	$16.3 \times$ "	1.29
"	"	"	0+	+	19.6^0	7 " "	0.506	$17.5 \times$ "	1.08
"	"	"	0+	+	16.8^0	8 " "	0.460	$15.8 \times$ "	0.82

TABLE 59

May 20, '20.

AMYL ALCOHOL

Mem-brane	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
6 Thick-ness S&S-589	Amyl Alco-hol	793.0	0	-	25.0°	5 m.m.	0.041	0.5×10^{-4}	0.33
"	"	"	0	-	29.5°	4.5" "	0.066	0.8 x "	0.29
"	"	"	0	-	35.0°	5 " "	0.066	0.8 x "	0.34
"	"	"	0	-	40.0°	5 " "	0.066	0.8 x "	0.35

TABLE 60

June 7, '20.

NITROBENZENE

Mem-brane	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
6 Thick-ness S&S-589	Nitro-ben-zene	555.0	0	+	20.4°	3.5m.m.	0.555	10×10^{-4}	0.55
"	"	"	0	+	25.5°	5 " "	0.686	12.3 x "	0.68
"	"	"	0	+	31.0°	3.5" "	0.708	12.7 x "	0.60
"	"	"	0	+	38.0°	3.5" "	0.788	14.1 x "	0.75

TABLE 61

June 16, '20.

PYRIDINE

Mem-brane Thick-ness	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
S&S-589	Pyri-dine "	841.0	1.0	+	26.5^{0}	3.5m.m.	0.085	9.8×10^{-5}	1.50
"	"	"	1.0	+	22.7^{0}	4.5" "	0.080	9.4 x "	1.42
"	"	"	0 +	+	19.2^{0}	6 " "	0.076	9.5 x "	1.50
"	"	"	0 +	+	30.0^{0}	7 " "	0.100	11.9 x "	1.57
"	"	"	0 +	+	35.0^{0}	4 " "	0.105	12.4 x "	1.50

TABLE 62

June 24, '20.

BENZALDEHYDE

n Mem-brane Thick-ness	Solu-tion	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
S&S-589	Benzal-dehyde "	954.0	0.5	+	20.5^{0}	6 m.m.	0.160	16.7×10^{-5}	0.81
"	"	"	0.5	+	25.0^{0}	7 " "	0.268	28.0 x "	0.88
"	"	"	0.5	+	31.0^{0}	6 " "	0.314	32.9 x "	0.85
"	"	"	0.5	+	37.0^{0}	6 " "	0.336	35.2 x "	0.93

TABLE 63

July 8, '20.

n-Butyl Alcohol

Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
6 Thickness 343-589	n-Butyl Alcohol	954.0	1.0	-	15.0°	4.5 m.m.	0.136	14.2×10^{-5}	0.54
"	"	"	1.0	-	20.5°	5 " "	0.164	17.1 x "	0.50
"	"	"	1.0	-	26.0°	5 " "	0.188	19.7 x "	0.57
"	"	"	1.0	-	31.0°	5 " "	0.195	20.4 x "	0.52
"	"	"	1.0	-	35.4°	4 " "	0.204	21.3 x "	0.55

For Table 57.

For Table 58.

For Table 59

For Table 60.

For Table 61

For Table 62.

For Table 63.

Rate of Osmose

Temperature.

The first acetone run, Table 57, was made using the same membrane throughout. This curve seemed to pass through a maximum. Thinking this might be caused by the use of a single membrane, a second trial was made, Table 58, changing the membrane and solvent for each run. The same type of curve was obtained, but careful examination showed that at high temperatures, bubbles formed in the apparatus, particularly the bubble tube. Also the indicator bubble increased greatly in size (above the point of safety) making such readings not acceptable. The remaining curves for amyl alcohol (Table 59), - nitrobenzene (Table 60), - pyridine (Table 61), - benzaldehyde (Table 62), - and n-butyl alcohol (Table 63), - are quite regular and like that for water. The temperature used was not high enough to cause the difficulty experienced with acetone, which has a comparatively low boiling point. Doubtless the others would be as erratic upon approaching the boiling point. The amyl alcohol shows a much more rapid change of endosmose rate with the first temperature change than any of the other solvents. An examination of the permeability rates which are recorded for each run shows that this could not account for any of the differences indicated.

THE EFFECT OF THE ADDITION OF CERTAIN SALTS

Very early in his work Perrin[96] stated his valence rule which was later taken up by most investigators and found to hold very well in water solutions. It was also shown to be true in the case of the lower alcohols.[97] Experiments were carried

96. Loc. cit.

97. Bandouin. Loc. cit. Barratt **. Harris. Loc. cit.

out to determine if such a relationship existed in the case of the
solvents under investigation. For cation effect the following
salts were used: $NaNO_3$; KNO_3; $Ca(NO_3)_2$; $Ba(NO_3)_2$; $Al(NO_3)_3$; $Cr(Ac)_3$;
$U(Ac)_4$; for anion effect: $KCNS$; $Cu(Ac)_2$; K_2SO_4; $K_2C_2O_4$; K_3PO_4;
Na_3Cit; $K_4Fe(CN)_6$.

In water, $N/1000$ solutions of most substances are completely
dissociated. As we have here lower dissociating media it was decided
to use $N/10000$ solutions. Furthermore, preliminary runs on acetone
gave too high a current reading in $N/1000$ solutions to make such
strength practical for the battery system used. The strength
$N/10000$ was quite easy to attain in most cases and in many, much
stronger solutions were possible. The salt was carefully weighed
and placed in a flask about 4/5 full of the solvent. This was
shaken vigorously and in some cases warmed. In a few instances,
as $Ca(NO_3)_2$ and $KCNS$, and in nearly all cases with pyridine as the
solvent, this was sufficient to get the salt into solution. In
most cases, however, the salt was crushed to a fine powder with a
long flat stirring rod, grinding and shaking until no visible par-
ticles remained. This, with subsequent warming, was sufficient
to dissolve the most difficultly soluble salts. It may be that
in some cases, as evidenced by no change in current reading, the
salts did not completely dissolve but remained in a sort of col-
lodial suspension, but all the solutions were perfectly clear
after standing over night. One of the reasons for choosing sol-
vents with a comparatively high dielectric constant was their high
dissociating power and hence their greater tendency to dissolve
electrolytes. Nitrates were chosen because of the erratic nature
of many of the chlorides and iodides toward solution in organic
solvents.

To determine which was the better concentration, N/10000 ·or M/10000, acetone solutions, were made up with each set of salts. Table 64 for the first set (cation effect) and Table 65 for the second set (anion effect) give the results for N/10000 concentration. Tables 66 and 67 show the corresponding effects using M/10000 solutions. No generalizations were possible from these results so it was decided to use N/10000 as being theoretically more comparative. If the effects were due to ion adsorption then only solutions of the same normality should be compared.

Tables 68 and 69 give the results with amyl alcohol; Tables 70 and 71, with nitrobenzene; Tables 72 and 73, with pyridine; Tables 74 and 75, with benzaldehyde; and Tables 76 and 77, with n-butyl alcohol. The data for the pure solvent is appended to each table to show the relationship.

TABLE 64

April 22, '20.

ACETONE

Membrane	Solution	Voltage	Current	Di-rection	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
Thickness	N/10000								
MS-589	NaNO$_3$	289.0	3-2	+	25°	5 m.m.	0.461	15.9 x 10^{-4}	1.12
"	" KNO$_3$	"	3-2	+	"	8 " "	0.488	16.9 x "	2.05
"	" Ca(NO$_3$)$_2$	"	1.5	-	"	7 " "	0.377	13.0 x "	0.80
"	" Ba(NO$_3$)$_2$	"	1 -	+	"	8 " "	0.803	27.7 x "	0.76
"	" Al(NO$_3$)$_3$	"	1	-	"	6 " "	0.127	4.2 x "	0.96
"	" Cr(Ac)$_3$	"	1 -	+	"	8 " "	1.258	46.9 x "	0.80
"	" U(ac)$_4$	"	0 +	+	"	5 " "	1.249	43.2 x "	0.02
"	Pure Solvent	"	0	+	"	5 " "	0.896	31.0 x "	0.77

TABLE 65

April 27, '20.

ACETONE

m Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S&S-589	N/10000 KCNS	289.0	5-6	+	25°	4.5m.m.	0.353	12.2 x 10⁻⁴	1.70
"	" Cu(Ac)₂	"	0 +	+	"	9 " "	0.728	25.1 x "	0.89
"	" K₂SO₄	"	0 +	+	"	7 " "	0.814	28.1 x "	0.87
"	" K₂C₂O₄	"	0 +	+	"	5 " "	0.887	30.6 x "	0.63
"	" K₃PO₄	"	0 +	+	"	4.5" "	0.744	25.7 x "	0.66
"	" Na₃Cit	"	0 +	+	"	8 " "	0.860	29.7 x "	1.00
"	" K₃Fe(CN)₆	"	0 +	+	"	4 " "	0.860	29.7 x "	0.68
"	Pure Solvent	"	0 +	+	"	4 " "	0.515	17.8 x "	0.83

TABLE 66

April 24, '20.

ACETONE

Mem-brane	Solution	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
8 Thick-ness	M/10000								
343-589 "	$NaNO_3$	289.0	3-2	+	25^0	6 m.m.	0.409	14.1×10^{-4}	0.80
"	" KNO_3	"	3	+	"	8 " "	0.498	17.0 x "	0.59
"	" $Ca(NO_3)_3$	"	1.5	-	"	4.5" "	0.198	6.8 x "	0.62
"	"$Ba(NO_3)_2$	"	1-	+	"	4.5" "	0.123	4.2 x "	0.73
"	"$Al(NO_3)_3$	"	1	-	"	8 " "	0.430	14.8 x "	0.61
"	"$Cr(Ac)_3$	"	1-	+	"	6 " "	1.796	62.1 x "	0.64
"	"$U(Ac)_4$	"	0+	+	"	8 " "	1.082	37.3 x "	0.74
"	Pure Solvent	"	0+	+	"	5.7" "	0.510	17.6 x "	0.73

TABLE 67

April 28, '20.

ACETONE

Mem-brane Thick-ness	Solution M/10000	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
848-589	" KCNS	289.0	5-3	+	25°	4.5m.m.	0.353	12.2×10^{-4}	1.70
"	" $Cu(Ac)_2$	"	0.5	+	"	5 " "	1.239	42.8 x "	0.75
"	" K_2SO_4	"	0.5	+	"	8 " "	1.123	38.8 x "	1.29
"	" $K_2C_2O_4$	"	1.5	+	"	6.5" "	0.919	31.8 x "	0.94
"	" $K_3P O_4$	"	2	+	"	4.5" "	1.203	41.6 x "	0.64
"	" Na_3Cit	"	1.5	+	"	9 " "	0.843	29.1 x "	0.74
"	" $K_4Fe(CN)_6$	"	1	-+	"	7 " "	0.703	24.3 x "	0.78
"	Pure Solvent	"	0+	+	"	8 " "	0.509	17.6 x "	2.42

TABLE 68

May 18, '20.

AMYL ALCOHOL

m Mem- o. brane	Solution	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
6 Thick- ness	1/10000								
S&S-589	" NaNO$_3$	623.0	0	-	25°	4.5m.m.	0.234	3.7 x 10^{-4}	0.30
"	" KNO$_3$	"	0	-	"	4.5" "	0.204	3.2 x "	0.28
"	" Ca(NO$_3$)$_2$	"	0	-	"	7.5" "	0.131	2.0 x "	0.29
"	" Ba(NO$_3$)$_2$	"	0	-	"	5.0" "	0.098	1.5 x "	0.30
"	" Al(NO$_3$)$_3$	"	0.5	-	"	5 " "	0.163	2.6 x "	0.29
"	" Cr(Ac)$_3$	"	0	-	"	4.5" "	0.063	1.0 x "	0.35
"	" U(Ac)$_4$	"	0	-	"	5.5" "	0.044	0.6 x "	0.38
"	Pure Solvent	"	0	-	"	7.5" "	0.158	2.5 x "	0.24

TABLE 69

May 20, '20.

AMYL ALCOHOL

Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
Thickness-N/10000									
843-589	" KCNS	623.0	1.0	-	25°	6 m.m.	0.261	4.1 x 10⁻⁴	0.33
"	" Cu(Ac)₂	"	0	-	"	6 " "	0.043	0.6 x "	0.32
"	" K₂SO₄	"	0	+	"	5 " "	0.014	0.2 x "	0.28
"	" K₂C₂O₄	"	0	-	"	4.5 "	0.016	0.2 x "	0.31
"	" K₃PO₄	"	0	-	"	4 " "	0.031	0.4 x "	0.31
"	" Na₃Cit	"	0	-	"	4.5 "	0.029	0.4 x "	0.27
"	" K₄Fe(CN)₆	"	0	-	"	5 " "	0.015	0.2 x "	0.25
"	Pure Solvent	"	0	-	"	7.5 "	0.158	2.5 x "	0.24

TABLE 70

June 3, '20.

NITROBENZENE

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
MS-589	N/10000 NaNO$_3$	555.0	0	+	25°	5.5m.m.	0.967	17.4 x 10^{-4}	0.57
"	" KNO$_3$	"	0	+	"	5.5" "	1.925	34.6 x "	0.62
"	" Ca(NO$_3$)$_2$	"	0	+	"	3 " "	0.965	17.3 x "	0.66
"	" Ba(NO$_3$)$_2$	"	0	+	"	5.5" "	0.641	11.5 x "	0.64
"	" Al(NO$_3$)$_3$	"	0	+	"	5 " "	1.464	26.3 x "	0.65
"	" Cr(Ac)$_3$	"	0	+	"	4.5" "	0.686	12.3 x "	0.65
"	" U(Ac)$_4$	"	0	+	"	6 " "	0.640	11.5 x "	0.58
"	Pure Solvent	"	0	+	"	6 " "	0.725	13.0 x "	0.58

TABLE 71

June 2, '20.

NITROBENZENE

Mem-brane Thick-ness	Solution	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
	N/10000								
588-589	" KCNS	555.0	0	+	25°	5.5m.m.	2.529	45.5 x 10⁻⁴	0.62
"	" Cu(Ac)₂	"	0	+	"	4 " "	0.478	8.6 x "	0.63
"	" K₂SO₄	"	0	+	"	4.5" "	0.648	11.6 x "	0.61
"	" K₂C₂O₄	"	0	+	"	3 " "	0.578	10.4 x "	0.65
"	" K₃PO₄	"	0	+	"	3 " "	1.006	18.1 x "	0.61
"	" Na₃Cit	"	0	+	"	4 " "	0.796	14.3 x "	0.58
"	" K₄Fe(CN)₆	"	0	+	"	5 " "	0.868	15.6 x "	0.62
"	Pure Solvent	"	0	+	"	6 " "	0.725	13.0 x "	0.68

TABLE 72

June 14, '20.

PYRIDINE

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S&S-589	" NaNO$_3$	841.0	4.0	-	26.5°	6 m.m.	0.481	57.1 x 10^{-5}	2.00
"	" KNO$_3$	"	1.5	-	"	4 " "	0.087	10.4 x "	1.81
"	"Ca(NO$_3$)$_2$	"	2.5	-	"	6 " "	0.192	22.8 x "	1.87
"	"Ba(NO$_3$)$_2$	"	1.0	+	"	5.5" "	0.061	7.2 x "	1.66
"	"Al(NO$_3$)$_3$	"	6.0	-	"	4 " "	0.352	41.8 x "	1.76
"	"Cr(Ac)$_3$	"	1.0	+	"	5 " "	0.081	9.6 x "	1.42
"	"U(Ac)$_4$	"	1.0	+	"	6 " "	0.212	25.2 x "	1.36
"	Pure Solvent	"	0	+	"	3.5" "	0.083	9.8 x "	1.50

TABLE 73

June 15, '20.

PYRIDINE

Mem-brane Thick-ness	Solution N/10000	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
S-589	" KCNS	841.0	7.0	-	26.5°	4 m.m.	0.973	115.5 x 10^{-5}		1.50
"	"Cu(Ac)$_2$	"	1.0	-	"	5.5" "	0.684	81.3 x "		1.87
"	"K$_2$SO$_4$	"	0	+	"	4 " "	0.120	14.2 x "		1.42
"	"K$_2$C$_2$O$_4$	"	1.0	+	"	6 " "	0.169	20 x "		1.66
"	"K$_3$PO$_4$	"	0	+	"	6 " "	0.095	11.2 x "		1.57
"	"Na$_3$Cit	"	1.0	+	"	6 " "	0.081	9.6 x "		1.87
"	"K$_4$Fe(CN)$_6$	"	1-	+	"	5 " "	0.099	11.7 x "		1.57
"	Pure Solvent	"	0	+	"	3.5" "	0.083	9.3 x "		1.50

TABLE 74

June 22, '20.

BENZALDEHYDE

m Mem-brane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
8 Thickness	N/10000								
S&S-589	" NaNO$_3$	954.0	1.0	-	25°	7 m.m.	0.185	19.3 x 10^{-5}	0.83
"	" KNO$_3$	"	1.0	+	"	7 " "	0.150	15.7 x "	0.86
"	"Ca(NO$_3$)$_2$	"	2.0	-	"	4 " "	1.522	159.5 x "	0.85
"	"Ba(NO$_3$)$_2$	"	1.0	-	"	6 " "	0.265	27.7 x "	0.93
"	"Al(NO$_3$)$_3$	"	1.5	+	"	6 " "	0.259	27.1 x "	0.85
"	"Cr(AC)$_3$	"	1.0	-	"	6.5" "	0.256	26.8 x "	0.93
"	"U(Ac)$_4$	"	2.0	-	"	6.5" "	0.593	62.1 x "	1.00
"	Pure Solvent	"	0.5	+	"	3 " "	0.297	31.0 x "	0.90

TABLE 75

June 23, '20.

BENZALDEHYDE

Membrane & Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S&S-589	KCNS	954.0	2.0	−	25°	4.5 m.m.	0.395	41.4 x 10⁻⁵	0.81
"	" Cu(Ac)₂	"	1.0	+	"	6 " "	0.173	18.1 x "	0.88
"	" K₂SO₄	"	0.5	+	"	4.5" "	0.168	17.6 x "	0.85
"	"K₂C₂O₄	"	1.0	+	"	5 " "	0.335	35.1 x "	0.83
"	"K₃PO₄	"	1.0	+	"	5 " "	0.610	63.9 x "	0.96
"	"Na₃Cit	"	0.5	+	"	7 " "	0.271	28.4 x "	0.90
"	"K₄Fe(CN)₆	"	1.0	+	"	4 " "	0.528	55.3 x "	0.83
"	Pure Solvent	"	0.5	+	"	3 " "	0.297	31.0 x "	0.90

TABLE 76

July 6, '20.

n-BUTYL ALCOHOL

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S&S-589	NaNO$_3$	954.0	3.0	-	26^{0}	6.5m.m.	0.358	37.5 x 10^{-5}	0.53
"	"KNO$_3$	"	2.0	-	"	4.5" "	0.464	48.6 x "	0.54
"	"Ca(NO$_3$)$_2$	"	1.5	-	"	3 " "	0.268	28.0 x "	0.50
"	"Ba(NO$_3$)$_2$	"	1.0	-	"	4 " "	0.158	16.5 x "	0.54
"	"Al(NO$_3$)$_3$	"	2.5	-	"	4 " "	0.268	28.0 x "	0.50
"	"Cr(Ac)$_3$	"	1.5	-	"	4 " "	0.247	25.8 x "	0.52
"	"U(Ac)$_4$	"	1.0	-	"	5.5" "	0.117	12.2 x "	0.51
"	Pure Solvent	"	1.0	-	"	5 " "	0.188	19.7 x "	0.57

TABLE 77

July 6, '20.

n-BUTYL ALCOHOL

m Mem-). brane	Solution	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
6 Thick- ness S&S-589	N/10000 " KCNS	954.0	3.5	-	26°	6 m.m.	0.619	64.8 x 10^{-5}	0.53
"	"Cu(Ac)$_2$	"	1.5	-	"	5.5" "	0.195	20.4 x "	0.54
"	"K$_2$SO$_4$	"	1.0	-	"	6 " "	0.117	12.2 x "	0.50
"	"K$_2$C$_2$O$_4$	"	1.0	-	"	5.5" "	0.120	12.5 x "	0.55
"	"K$_3$PO$_4$	"	1.5	-	"	4.5" "	0.421	44.1 x "	0.51
"	"Na$_3$Cit	"	1	-	"	5.5" "	0.114	11.9 x "	0.55
"	"K$_4$Fe(CN)$_6$	"	1.5-	-	"	5.5" "	0.115	12.0 x "	0.53
"	Pure Solvent	"	1.0	-	"	5 " "	0.188	19.7 x "	0.57

Some very interesting things were noted during these runs. It will be seen that the flow is not always in the same direction with the substances dissolved as with the pure solvent. Further, the flow is sometimes greater and sometimes less with the same type of solute. For example, Table 64 shows nearly all having a slower rate, except for Cr and U salts, while in Table 65 all manifest a faster rate than the pure acetone. This is also evident in other tables. Table 69 holds fairly well for the valence rule, except for the bivalent cation, as does Table 76. However, in most cases there is no such generalization possible. Nor can differences in permeability explain these results.

Further, the same cation or anion has not the same effect upon the endosmose in different solvents. The presence of various salts in organic solvents has a great effect upon the electrolysis products. Unlike water these solvents enter into chemical combination with a great many salts. Both of these effects would produce ions of a nature not evidenced by the salts used. These ions may possess a high or low adsorptive factor. The substances produced thus may act upon the membrane itself, so there is a multiplicity of factors of which only a few can be studied.

THE EFFECT OF VARYING THE CONCENTRATION OF THE SALT
IN SOLUTION

Earlier workers with water solutions found a maximum endosmose effect at a definite concentration of the dissolved salt. Loeb[98], in his very recent investigation, noted this same

98. Loc. cit.

effect in both electric and "free osmosis". In an unpublished thesis[99a] written some four years ago the author made the statement that any solution when sufficiently dilute would give positive endosmose (toward the cathode). This work was all with water. It seems necessary to qualify this statement to say that any solution if sufficiently dilute will flow, under a potential gradient, in the direction exhibited by the pure solvent.

To test this statement concentration runs were made with each solvent. That salt was selected which had the highest solubility is the solvent in question. A N/100 solution was made and successively diluted to N/1000, N/10000, N/100000, and N/1000000. These were then run keeping other factors constant. Like the acid-alkali runs the least concentrated were used first with a new membrane for each change. Permeability runs did not show this a disturbing factor.

The results are shown in the following tables and curves where the rate of endosmose is plotted against the concentration of the salt.

Table 78 is for acetone + $Ca(NO_3)_2$, Table 79 for acetone + $Na\ NO_3$, Table 80 for amyl alcohol + KCNS, Table 81 for nitrobenzene + $Ca(NO_3)_2$, Table 82 for pyridine + $Ca(NO_3)_2$, Table 83 for benzaldehyde + KCNS, and Table 84 for n-butyl alcohol + $Ca(NO_3)_2$.

99a. A.Strickler - M.S.Thesis, Univ. of Michigan (1915).

TABLE 78

May 5, '20.

ACETONE

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
S&S-589	$Ca(NO_3)_2$ N/100 "	287.0	8-6	-	25^0	6 m.m.	0.098	3.4×10^{-4}
"	N/1000 "	"	2	-	"	6 " "	0.141	4.9 x "
"	N/10000 "	"	1.5	-	"	6 " "	0.257	8.9 x "
"	N/100000 "	"	1.0	+	"	6 " "	0.049	1.7 x "
"	N/1000000 "	"	0.5	+	"	6 " "	0.955	33.3 x "

TABLE 79

May 6, '20.

ACETONE

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S&S-589	$NaNO_3$ N/1000 "	287.0	12.0	+	25^0	6 m.m.	0.062	2.1×10^{-4}	0.87
"	N/10000 "	"	2.0	+	"	6 " "	0.264	9.1 x "	1.24
"	N/100000 "	"	1.5	+	"	5 " "	0.175	6.0 x "	0.95
"	N/1000000 "	"	0.5	+	"	7 " "	0.121	4.1 x "	0.85

TABLE 80

May 25, '20.

AMYL ALCOHOL

Mem-brane Thick-ness	Solution KCNS	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
3&S-589	N/1000000 "	623.0	0	-	25°	7.5m.m.	0.058	0.9×10^{-4}	0.36
"	N/100000	"	0	-	"	6.5" "	0.088	1.4 x "	0.37
"	N/10000	"	0.5	-	"	5 " "	0.243	3.9 x "	0.44
"	N/1000	"	8.5	-	"	4.5" "	0.238	3.8 x "	0.39
"	N/100	"	12.0	-	"	4.5" "	0.180	1.9 x "	0.44

TABLE 81

June 4, '20.

NITROBENZENE

Mem-brane Thick-ness	Solution Ca(NO$_3$)$_2$	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
3&S-589	N/100 "	555.0	0	+	25°	5 m.m.	1.108	19.9×10^{-4}	0.58
"	N/1000 "	"	0	+	"	3 " "	0.820	14.7 x "	0.61
"	N/10000 "	"	0	+	"	3 " "	0.965	17.3 x "	0.66
"	N/100000"	"	0	+	"	5 " "	0.577	10.3 x "	0.50
"	N/1000000"	"	0	+	"	3.5 "	0.633	11.4 x "	0.57

TABLE 82

June 15, '20.

PYRIDINE

Membrane Thickness	Solution	Voltage	Current	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
48-589	Ca(NO$_3$)$_2$ N/1000000 " 841.0	0.5	+	26.5°	5 m.m.	0.046	5.4 x 10^{-5}	1.42	
"	N/100000 " "	1.0	+	"	5 " "	0.010	1.1 x "	1.76	
"	N/10000 " "	2.0	-	"	5.5" "	0.142	16.8 x "	1.66	
"	N/1000 " "	4.0	-	"	6. " "	0.130	15.4 x "	1.50	
"	N/100 " "	8.0	-	"	3 " "	0.109	12.9 x "	1.76	

TABLE 83

June 23, '20.

BENZALDEHYDE

Membrane Thickness	Solution	Voltage	Current	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
48-589	KCNS N/1000000 " 954.0	1.0	+	25°	6 m.m.	0.220	23.2 x 10^{-5}	0.93	
"	N/100000 " "	1.0	-	"	6.5" "	0.051	5.3 x "	0.88	
"	N/10000 " "	2.0	-	"	7 " "	0.394	41.3 x "	0.90	
"	N/1000 " "	13.0	-	"	5 " "	0.615	64.4 x "	0.96	
"	N/100 " "	60.0	-	"	6 " "	0.083	8.7 x "	0.88	

TABLE 84

July 7, '20.

n-BUTYL ALCOHOL

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
48-589	Ca(NO$_3$)$_2$ N/1000000 "	954.0	1.0	-	26°	5 m.m.	0.107	11.2 x 10^{-5}	0.53
"	N/100000 "	"	1.0	-	"	6 " "	0.150	15.7 x "	0.51
"	N/10000 "	"	1.5	-	"	5.5" "	0.224	23.4 x "	0.55
"	N/1000 "	"	2.0	-	"	3.5" "	0.194	20.3 x "	0.50
"	N/100 "	"	5.5	-	"	6 " "	0.128	13.4 x "	0.52

For Table 78.

To Anode ←   → To Cathode

Rate of Osmose.

For Table 79

Rate of Osmose

For Table 80

Rate of Osmose

For Table 81.

Rate of Osmose

For Table 82.

To Cathode ← → To Anode

Rate of Osmose

$\frac{N}{100000}$ $\frac{N}{10000}$ $\frac{N}{1000}$ $\frac{N}{100}$

.05 0 .05 .10 .15

For Table 83.

To Cathode ← → To Anode

Rate of Osmose.

$\frac{N}{100000}$ $\frac{N}{10000}$ $\frac{N}{1000}$ $\frac{N}{100}$

.04 .02 0 .02 .04 .06 .08

For Table 84.

Rate of Osmose.

$\frac{N}{100000}$ $\frac{N}{10000}$ $\frac{N}{1000}$ $\frac{N}{100}$

.10 .11 .12 .13 .14 .15 .16 .17 .18 .19 .20 .21 .22 .23

A striking similarity is seen in the curves, all but benzaldehyde (which was doubtless due to oxidation effects) exhibiting a maximum. Also in every case where the endosmose with the salt in solution gave a reverse flow to that of the pure solvent (Tables 78, 82 and 83) at very low concentrations this became regular again. The point where the curve crosses the zero line represents the isoelectric point of no flow for that particular salt in a particular solution with the particular membrane used and under the conditions of working. At such a concentration there are just enough adsorbed ions present to neutralize the contact charge on the membrane.

In many cases the current ran up pretty high in the more concentrated solutions, but no electrolysis effects were noted during the time of flow. A comparison of these curves with the acid-alkali curves shows that they have this same maximum and at approximately the same concentration.

THE EFFECT OF ADDED WATER

Because all readings were taken with the apparatus in a water bath, with the consequent possibility of water leaking in, and though the substances used were as nearly anhydrous as possible, it seemed advisable to make a series of runs with varying percentages of water added. Such experiments were carried out, first noting the effect upon the pure solvent and then upon the solvent containing a dissolved salt. Water was not sufficiently miscible with nitrobenzene or benzaldehyde to permit of such measurements. Every attempt was made to keep

other factors constant. Marked heating effects were noted when
making the higher concentrated solutions of water in acetone and
pyridine. It was also found difficult under these conditions to
remove all the air bubbles from the membrane. The combination of
water and non aqueous solution seemed to hold these tiny air
bubbles very tenaciously. Repeated soaking and rinsing was neces-
sary in every case and this also applied to the higher concentra-
tions of water in amyl and n-butyl alcohols.

The results obtained are shown in the following tables
and curves. For the curves, rate of endosmose is plotted against
percentage of water added.

TABLE 85

May 1, '20.

ACETONE

Mem-brane	Solu-tion % H₂O added	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
348-589	0	289.0	0+	+	24°	4.5 m.m.	0.600	20.7 x 10⁻⁴	0.80
"	1	"	0+	+	"	5.5 " "	0.387	13.3 x "	0.98
"	5	"	0.5	+	"	7 " "	0.371	12.8 x "	0.76
"	10	"	1-	+	"	7 " "	0.248	8.5 x "	1.12
"	20	"	2.0	+	"	5 " "	0.172	5.9 x "	2.66
"	100	"	2.0	+	"	4 " "	0.111	3.8 x "	1.35

TABLE 86

May 4, '20.

ACETONE + 10000 NaNO₃

Mem-brane	Solu-tion % H₂O added	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
348-589	0	289.0	3.2	+	25°	7 m.m.	0.431	14.9 x 10⁻⁴	1.35
"	0.5	"	3.2	+	"	6 " "	0.252	8.7 x "	0.90
"	1.0	"	2	+	"	7 " "	0.492	17.0 x "	1.02
"	5.0	"	3	+	"	7 " "	0.232	8.0 x "	0.82
"	10.0	"	4	+	"	8 " "	0.135	4.6 x "	0.95
"	20.0	"	4	+	"	6 " "	0.129	4.4 x "	2.75
"	50.0	"	4.5	+	"	4 " "	0.091	3.1 x "	2.75
"	100.0	"	5.8	+	"	4.5 " "	0.696	24.0 x "	1.45

TABLE 87

May 22, '20.

AMYL ALCOHOL

Mem- brane Thick- ness	Solu- tion %H$_2$O added	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
48-589	0	793.0	0	-	25°	5 m.m.	0.041	0.5 x 10^{-4}	0.28
"	0.5	"	0	-	"	5.5" "	0.020	0.2 x "	0.30
"	1.0	"	0	-	"	6 " "	0.012	0.1 x "	0.29
"	2.0	"	0	-	"	6 " "	0.010	0.1 x "	0.28
"	5.0	"	0	✦	"	4.5" "	0.009	0.1 x "	0.29
"	8.0	"	0	+	"	6.5" "	0.011	0.1 x "	0.35
"	100.0	"	11.0	+	"	7.5" "	0.513	6.4 x "	1.00

TABLE 88

May 24, '20.

AMYL ALCOHOL + N/10000 NaNO$_3$

Mem- brane Thick- ness	Solu- tion %H$_2$O added	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea- bility
48-589	0	623.0	0	-	25°	3.5m.m.	0.254	4.0 x 10^{-4}	0.44
"	0.5	"	0.5	-	"	5 " "	0.258	4.1 x "	0.36
"	1.0	"	1.0	-	"	5 " "	0.217	3.4 x "	0.27
"	5.0	"	1.5	+	"	6 " "	0.009	0.1 x "	0.34
"	7.0	"	1.5	+	"	6.5" "	0.019	0.3 x "	0.29
"	100.0	"	14.0	+	"	4.5" "	0.167	18.7 x "	1.33

TABLE 89

June 16, '20.

PYRIDINE

Mem-brane Thickness	Solu-tion % H₂O added	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
348-589	0	841.0	0.5	+	26.5°	6 m.m.	0.083	9.8 x 10⁻⁵	1.15
"	0.5	"	0.5	+	"	5.5" "	0.063	7.4 x "	1.20
"	1.0	"	1.0	+	"	5.5" "	0.072	8.5 x "	1.03
"	5.0	"	1.0	+	"	6 " "	0.073	8.6 x "	1.36
"	10.0	"	1.0+	+	"	6 " "	0.190	22.6 x "	1.13
"	25.0	"	4.0	+	"	5 " "	0.289	34.3 x "	1.20
"	50.0	"	7.0	+	"	4 " "	0.390	46.3 x "	0.90
"	100.0	"	18.0	+	"	6 " "	0.518	61.5 x "	2.00

TABLE 90

June 16, '20.

PYRIDINE + N/10000 KCNS

Mem-brane Thickness	Solu-tion % H₂O added	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
348-589	0	841.0	7.0	-	26.5°	4 m.m.	0.973	115.5 x 10⁻⁵	1.50
"	0.5	"	6.0	-	"	6 " "	0.551	65.5 x "	1.17
"	1.0	"	6.0	-	"	5.5" "	0.333	39.5 x "	1.25
"	5.0	"	11.0	-	"	3.5" "	0.057	6.7 x "	1.11
"	10.0	"	8.0	+	"	5 " "	0.213	25.3 x "	1.17
"	25.0	"	8.0	+	"	3 " "	0.250	29.7 x "	0.90
"	50.0	"	20.0	+	"	5 " "	0.285	33.8 x "	1.06
"	100.0	"	24.0	+	"	6 " "	0.360	42.8 x "	1.76

TABLE 91

July 7, '20.

n BUTYL ALCOHOL

Mem-brane Thick-ness	Solu-tion % H₂O added	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
48-589	0	954.0	1.0	-	26°	5 m.m.	0.188	19.7 x 10⁻⁵	0.57
"	0.5	"	1.0	-	"	5.5" "	0.102	10.6 x "	0.52
"	1.0	"	1.0	-	"	5.5" "	0.072	7.5 x "	0.54
"	2.0	"	1.0	-	"	6 " "	0.065	6.8 x "	0.51
"	5.0	"	1.5	-	"	5.5" "	0.040	4.1 x "	0.52
"	8.0	"	2.0	+	"	5 " "	0.019	1.9 x "	0.53
"	100.0	841.0	18.0	+	"	6 " "	0.518	61.5 x "	2.00

TABLE 92

July 7, '20.

n-BUTYL ALCOHOL + N/10000 KCNS

Mem-brane Thick-ness	Solu-tion % H₂O added	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
848-589	0	954.0	3.5	-	26°	6 m.m.	0.619	64.8 x 10⁻⁵	0.53
"	0.5	"	3.5	-	"	3 " "	0.426	44.6 x "	0.53
"	1.0	"	3.5	-	"	5.5" "	0.412	43.1 x "	0.60
"	2.0	"	3.5	-	"	6 " "	0.292	30.6 x "	0.54
"	5.0	"	5.0	-	"	6 " "	0.124	12.9 x "	0.49
"	8.0	"	5.0	+	"	5 " "	0.030	3.1 x "	0.52
"	100.0	"	24.0	+	"	6 " "	0.360	42.8 x "	1.76

For Table 87.   For Table 88.

To Anode ← → To Cathode   To Anode ← → To Cathode

Rate of Osmose   Rate of Osmose

For Table 89.

For Table 90.

Rate of Osmose.

Rate of Osmose.

Anode → Cathode

For Table 91.

For Table 92.

Anode | → To Cathode

Anode | → To Cathode

Rate of Osmose.
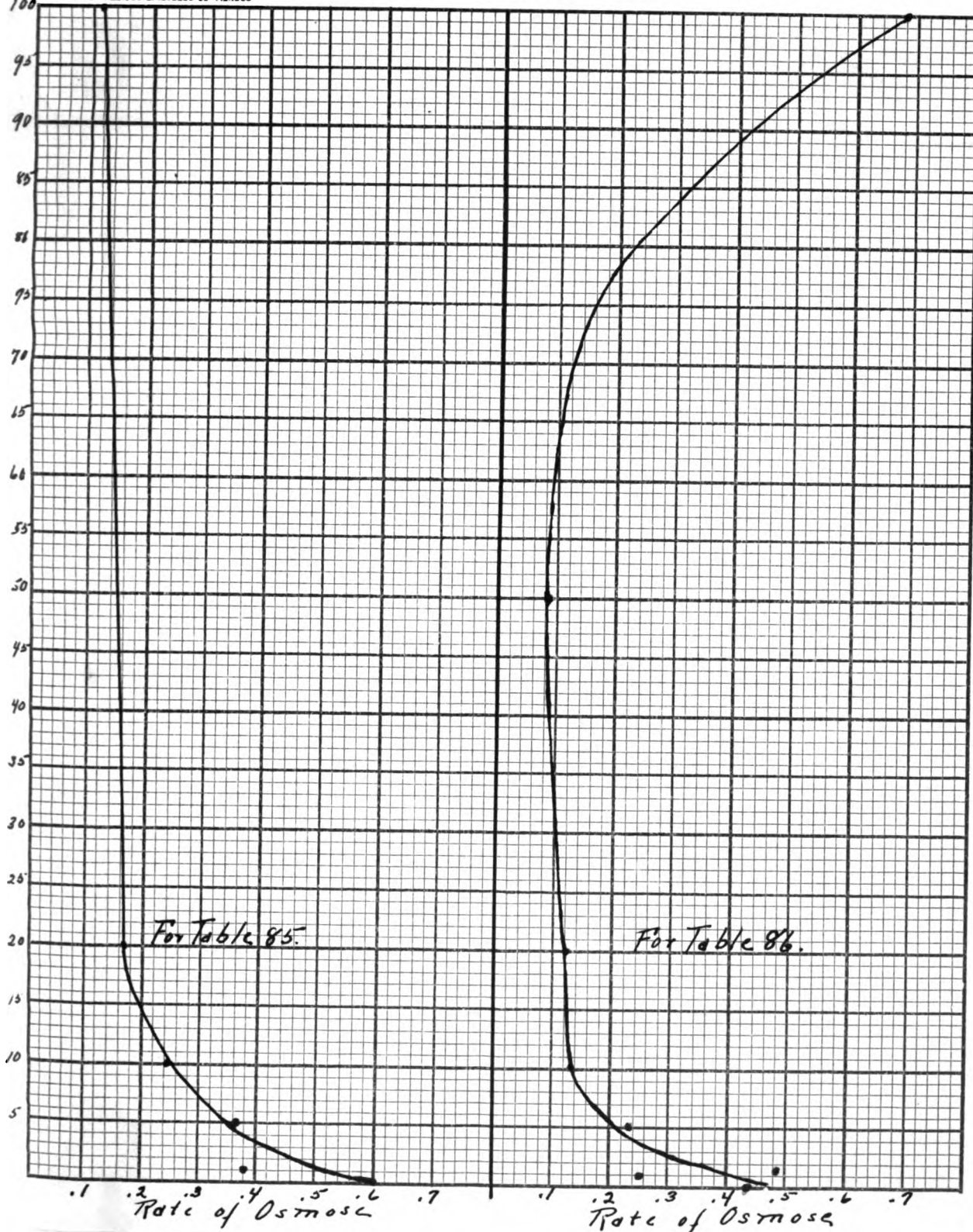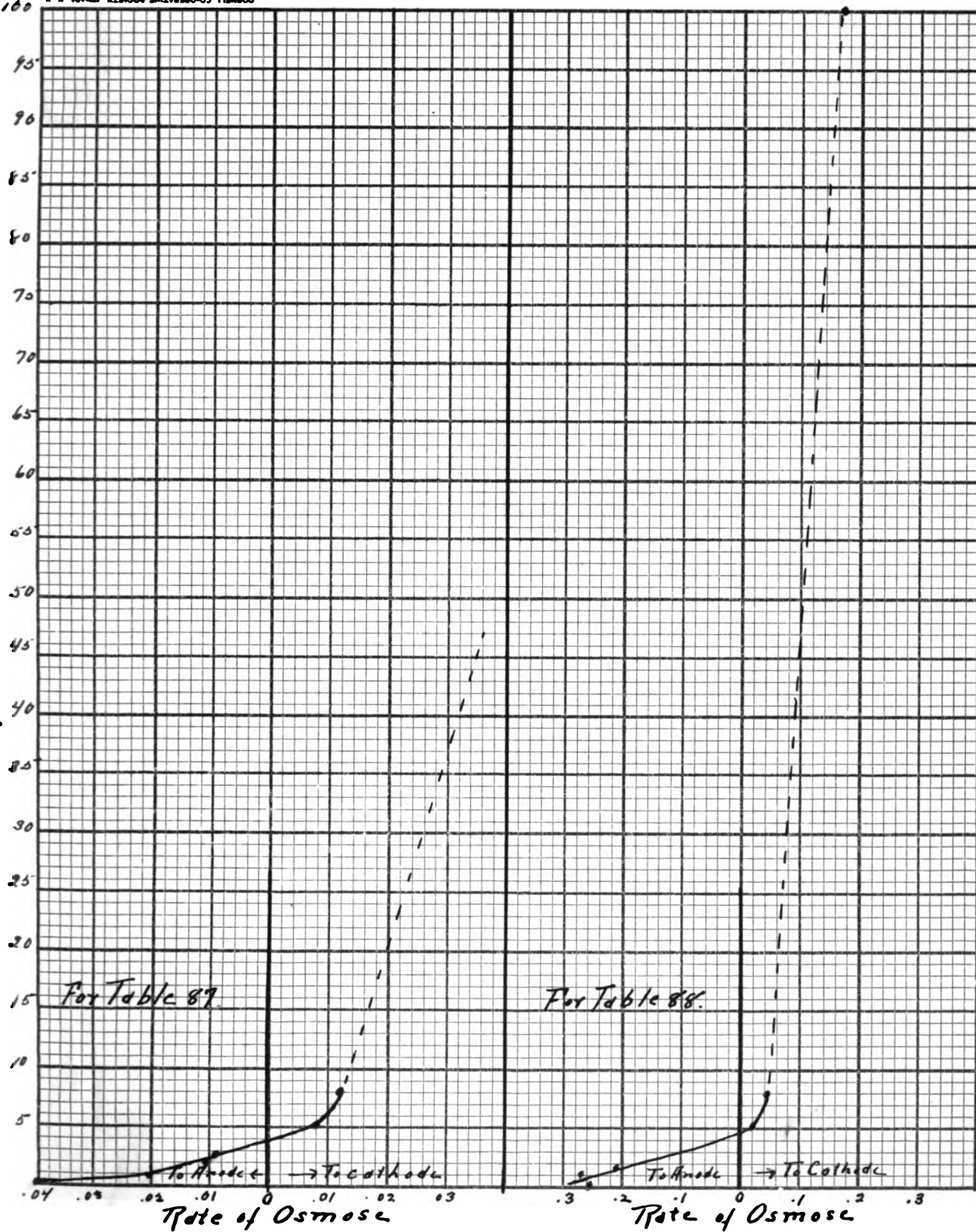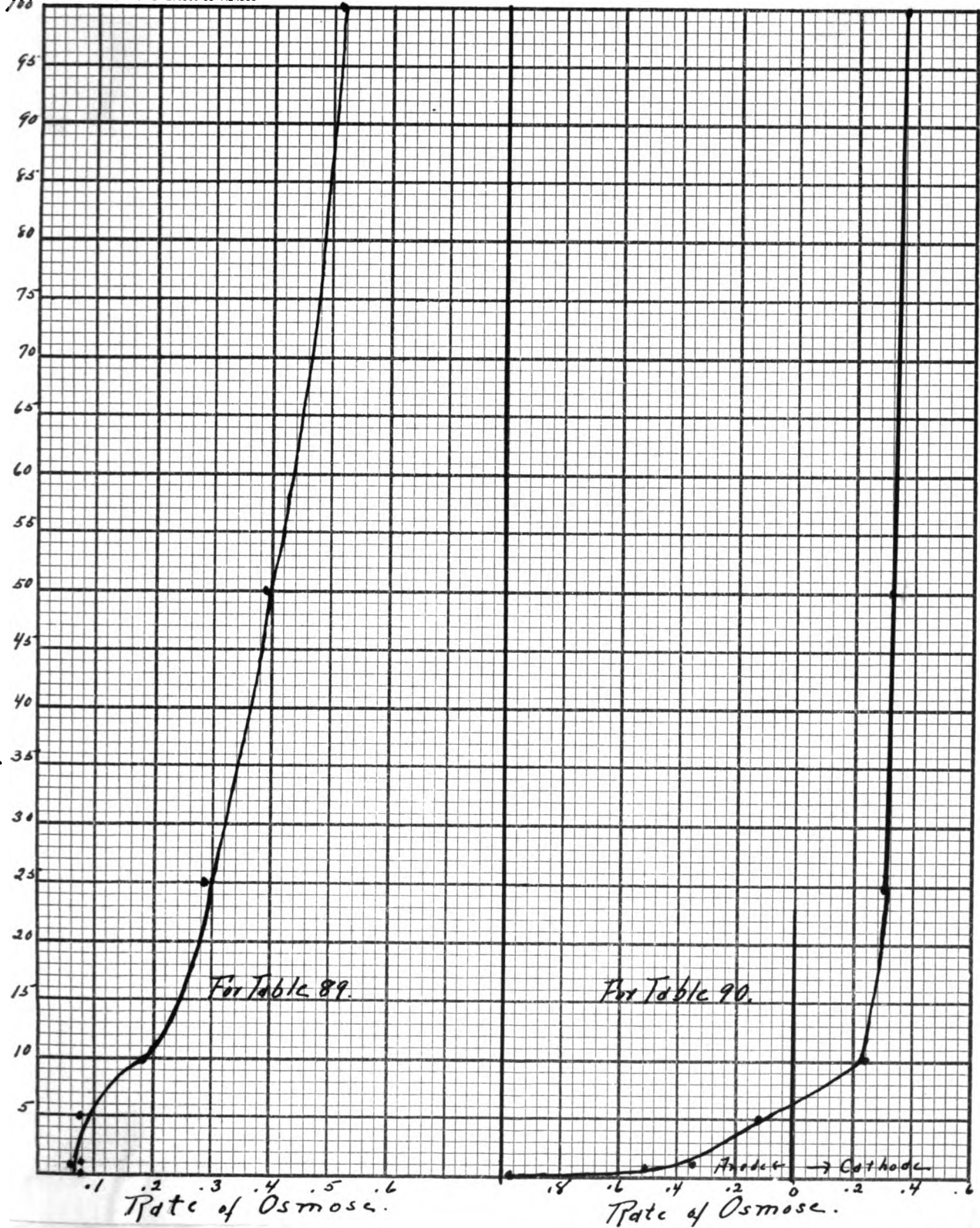
Rate of Osmose.

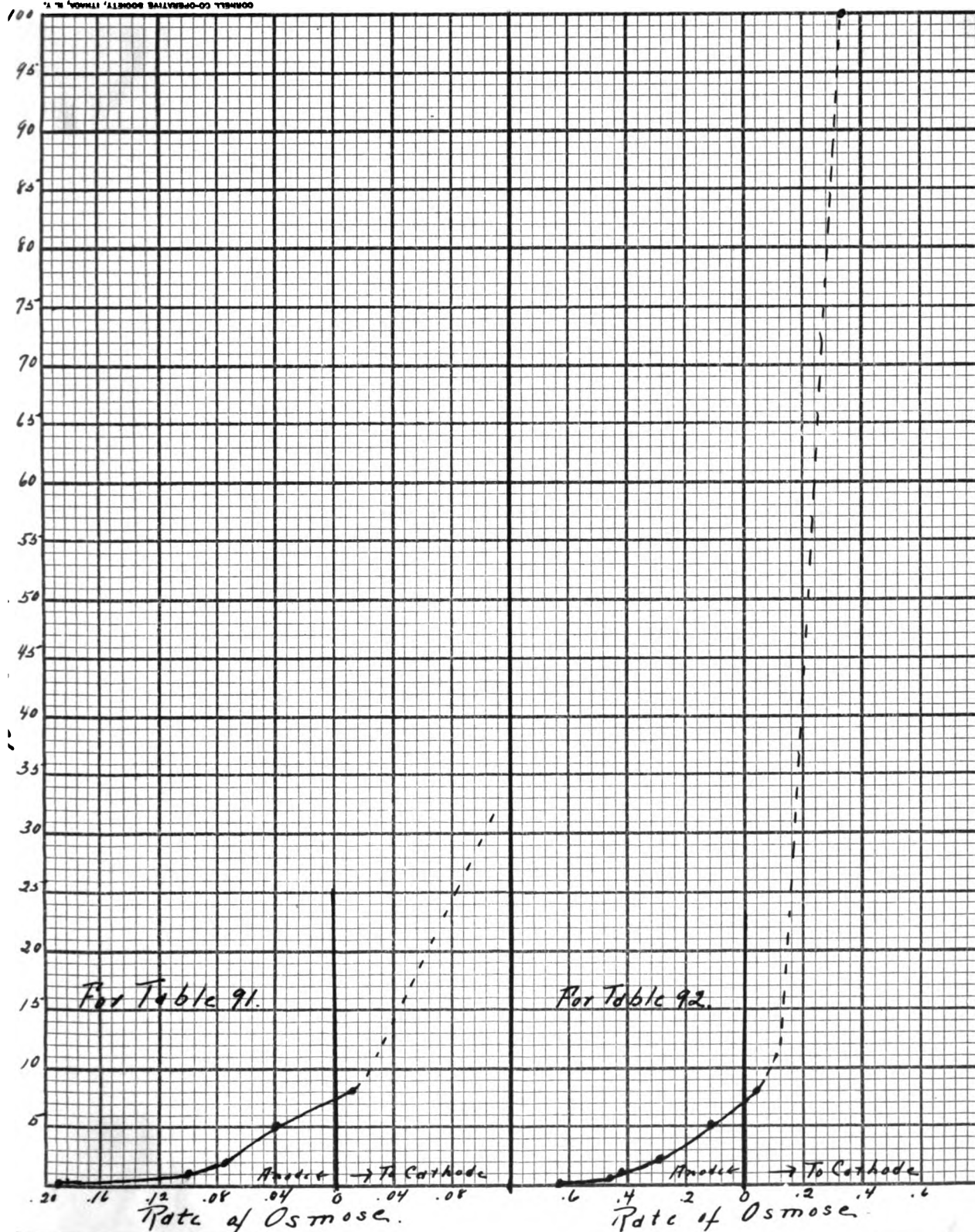Table 85 and its curve are for pure acetone and Table 86 for acetone containing N/10000 Na NO₃. The curves are very similar at low concentrations, there being a gradual decrease in the rate of endosmose with an increase in water content. But while the endosmose with pure water is less than acetone, *that with* water + N/10000 NaNO₃ is much greater even than the same concentration in acetone. A change in viscosity due to added water would explain the first but certainly other factors are effective in the second case. Here, as in all the other cases, the first quantities of added water manifest the greatest effects.

Pure amyl alcohol is shown in Table 87 and amyl alcohol + N/10000 NaNO₃ in Table 88. As this solvent is not very miscible with water, only low percentages of water could be tried. The data for pure water is added for comparison though a curve drawn above 8% has no meaning. While both solvent and solution gave negative endosmose, a small percentage of water reversed the flow. If the behavior of pure amyl alcohol was due to occluded acid, as at first thought, the water would not tend to reverse, as H ions would affect it in the same direction.

With pyridine, Table 89, there is a gradual increase of flow with increasing water content, which might again be explained by viscosity changes. But with pyridine + N/10000 KCNS (Table 90), where the endosmose is negative, added water decreased the flow through zero and then manifested an increase of positive endosmose up to that of pure water + N/10000 KCNS. There is evidently shown here a difference in the relative adsorption of the ions in water and pyridine.

n-Butyl alcohol, Table 91, for the pure solvent, and
Table 92 for the solvent + N/10000 KCNS, is quite like that for amyl
alcohol and is explained in the same manner.

RUNS ON ORGANIC SOLVENTS OF VARYING DIELECTRIC CONSTANTS

Because early writers on electric endosmose found many
substances which did not manifest endosmotic flow, it was decided
to try out several of these and others. Most of the substances
listed as showing no movement were substances with a low dielectric
constant. And as the endosmotic flow was found to be nearly pro-
portional, directly, to the applied voltage, it seemed probable
that these would also exhibit such effects if the voltage were
high enough. The substances chosen are listed in Table 93.

All of these solvents were dehydrated and purified
carefully by accepted methods and final fractional distillation.
Some of them were prepared by the author's students in organic
chemistry. The formamide was a purified sample secured from
Dr. V. L. Bohnson and the propyl alcohol and esters were some that
had been purified by Dr. J. H. Mathews. The same thickness of
membrane was used in each case but it will be seen that the
permeability rate varied considerably, doubtless affecting the
rate of endosmotic flow. Formamide was too good a conductor to
secure a reading without harming the battery system.

Those of low dielectric constant (Landolt, Börnstein)
did show a slow rate, but if we accept that for the membrane
(cellulose) as 2.5, Coehn's rule[99] does not hold in every case

99. Loc. cit.

even for the pure solvent. Therefore, though the dielectric constant ratio undoubtedly has a bearing upon the magnitude of the flow, the direction is probably determined by other factors which are much more important.

TABLE 93

May 27 and June 9, '20.

VARIOUS ORGANIC SOLVENTS

Membrane Thickness	Solution	Voltage	Current	Direction	Temp.	D.	Bubble	cm/sec Osmose	cm/sec Permeability
48-589	Benzene	978.0	0	-	25°	2.3	5 m.m.	0.0009	1.92
"	Xylene	"	0	-	"	2.37	7 " "	0.0006	1.92
"	Ether	"	0	+	"	4.4	7.5" "	0.0011	1.92
"	Chloroform	"	0	+	"	5.0	6.5" "	0.0038	3.33
"	CS_2	"	0	+	"	2.6	5 " "	0.0007	5.00
"	Amylene	"	0	+	"	2.2	6 " "	very slight	
"	Propyl Alcohol	"	2.0	+	"	11-22	4.5" "	0.077	0.57
"	Propionic Acid	"	0	+	"	3-5	4.5" "	very slight	
"	Formanide	55.0	300.0+	-	"	84.0	3 " "	------------	
"	Allyl Alcohol	555.0	6	-	"	20.6	6 " "	0.00068	----
"	Toluene	971.0	0	-	"	2.355	5.5" "	0.0012	2.40
"	Diethyl Aniline	"	0	+	"	-	4 " "	0.0067	0.40
"	Aniline	"	0	+	"	7.2	4 " "	0.074	0.25
"	Isobutyl Formate	"	0	-	"	7.28	5 " "	0.122	1.36
"	Isoamyl Formate	"	0	-	"	5.61	7 " "	0.053	1.50
"	Ethyl Propionate	"	0	+	"	5.64	4.5" "	0.483	2.14
"	Propyl Propionate	"	0	+	"	-	8 " "	0.129	1.25
"	Ethyl Isobutyrate	"	0	+	"	5.08	4 " "	0.012	2.06
"	Isobutyl Acetate	"	0	+	"	5.26	5 " "	0.034	1.25

THEORETICAL DISCUSSION

When an attempt is made to assemble all the factors
effective in electric endosmose, one finds it possible only to
consider those of greatest importance. We have here a membrane
in contact with a solution and, during the flow, this solution
also passing through the pores of the membrane. Hence, any thing
which will alter the membrane, the solution, the conditions caus-
ing the flow, or the condition at the surface of contact of the
solution and membrane, will affect the rate at which it will pass
through such membrane. The variation of push or pull would be
measured by the voltage change.

Very early in the study of this phenomenon, it was seen
(Introduction) that the conditions at the contact of membrane and
solution had much to do with it. Any solid medium in contact with
a liquid medium was found by Quincke and Helmholtz[100] to possess
at its surface of contact an electrical double layer established
merely by such contact. Later, Coehn[101] noted that this charge
seemed to be directly related to the dielectric constant ratio
of the two media, the substance having the higher dielectric
constant bearing the positive charge. Many exceptions were found
to this rule especially in the case where electrolytes were
present. This was explained rightly by Freundlich and Bancroft[102]
on the basis of adsorption. Any surface will tend to adsorb both

100. Loc. cit.

101. Loc. cit.

102. Loc. cit.

the solvent and the substances in solution. If the molecule was
adsorbed it should have no effect,[103] but if the ion, it would
increase or decrease the charge on the membrane depending upon
which ion was adsorbed most and what the original charge on the
membrane was. As practically all previous work was done with
water solutions, where most membranes bear a negative charge,
the flow would be increased or decreased depending upon whether
the anion or cation was adsorbed most.

The amount of adsorption is determined by the nature of
the membrane surface[104] which manifests a preferential or relative
adsorption for the various ions in solution. It is this which
determines the amount of charge and hence the rate of flow.
There is no question as to the very important effect of ion
adsorption upon the already charged membrane. But there seems
as yet no adequate explanation as to how the membrane acquires
this original charge. Briggs,[105] following Freundlich and Ban-
croft, said that it was purely an adsorption phenomenon. The
effective charge was produced by the ionization of the water with
subsequent preferential adsorption of the OH ion and the solution
of the membrane which might also produce highly adsorbed ions.
In the light of the work on non aqueous solvents, it can be seen
how the very low ionization, coincident with a low dielectric
constant, might produce few ions and a small charge on the membrane.

103. Loc. cit.

104. Loc. cit.

105. Loc. cit.

In many cases the effects were greater in the nonaqueous solvent than in water. But the direction as shown by amyl alcohol, n-butyl alcohol and many substances in Table 93 does not conform to Coehn's rule. Even this might be explained by the production of a preferentially highly adsorbed ion, in these cases a positive ion which would produce a positive charge on the membrane.

However, such assumptions do not seem necessary in the light of Langmuir's work[106] on thin films. Organic substances as well as water can be considered as possessing polar qualities. When these molecules are adsorbed at the surface of the membrane, this including the inner surface of the pores, they become oriented and thus produce the charge on the membrane. This orientation depends both upon the solvent and the membrane, as the molecules of a solvent may orient themselves differently at the surface of contact with different membranes. The quantity of charge would depend upon the amount of adsorption, as in the former theory of Briggs. The solution in the immediate vicinity would possess an opposite charge and hence the establishment of a potential gradient would cause migration of the movable medium. Adsorbable ions in solution would have the same effect upon the charged membrane. Further, most solvents arrange themselves at the surface of contact in such a way as to comply with Coehn's dielectric constant ratio rule, but many do not. No present objection is seen to such a supposition and it is submitted with such proof as is here outlined and with the idea of continuing this study in the near future.

106. Langmuir's Papers. J. Am. Chem. Soc., 38,1860; 1917.

Let us consider the data as given in this paper. It should be noted at the outset that water is a unique substance and that theories relating thereto must often be modified before application to non aqueous solvents. While most substances are fairly soluble in water, many exhibit complete insolubility in organic solvents. Furthermore, if they do go into solution, they may have absolutely no effect upon the current as shown with practically every solvent used. This might mean either chemical reaction or that they were still in the molecular condition to a large extent. But these same substances did affect the endosmotic flow either due to selective adsorption of the very few ions produced or to an adsorption of the molecule itself with consequent orientation. Also there is a possibility of the production of a variety of substances, mostly oxidation products, by the electrolysis of the organic substances. A very small amount, which might be greatly enhanced by a salt in solution, might give a substance wholly different in its effect during endosmotic flow. (Note the curves for continuous runs Tables 2 to 8). For example: an alcohol would tend to produce an acid, which might in part explain the behavior of amyl and n-butyl alcohols were it not for the fact that methyl[107] and ethyl[108] alcohols were perfectly regular.

Let us recall the accepted formulae for electric endosmose flow: ($V = \frac{q \cdot KD}{4\pi\eta l}$), as discussed in the introduction. There is no factor in this equation which might be considered as measuring the permeability of the membrane used. Tables 9 to 27 include

107. Bandouin, Loc. cit.

108. Barratt and Harris. Loc. cit.

one of the most important contributions in this paper. Nearly all
the work on electric endosmose has been carried out on the suppo-
sition that the thickness of the membrane had no effect and this
was expressly asserted by Bethe and Toropoff.[109] Quincke[110] did
say, "the smaller the pore, the greater the endosmose," but with
Wiedemann[111] concluded that "the flow is independent of the area
or thickness of the porous wall." The extreme regularity of the
curves shows that this is a factor which cannot be neglected.
It might be suggested that, as the adsorption curve of concentra-
tion is parabolic in form, this might partially explain the rela-
tionship between permeability and rate of endosmose. As the mem-
brane particles increase in concentration in contact with the
solution, the effects would tend to increase up to a maximum
and then decrease as the adsorption effect does with increasing
concentration of adsorbed substances. However, the fact remains
that permeability is a factor, whatever it measures, which must
be taken into account in all endosmotic readings. Also, the
uniformity would be greater with membranes possessing the same
permeability, other factors being equal. This might account for
some of the peculiar phenomena of "free osmosis". Whether this
factor should be included in the equation is a matter not yet settled.

Tables 28 to 41 show that it is possible to duplicate
conditions by the use of similar membranes of filter paper to
such an extent that the endosmose rate is duplicated. This greatly
increases the possibility of rapid determination of endosmotic

109. Loc. cit.

110. Loc. cit.

111. Loc. cit.

measurements. The difficulty noted in the case of water might be due to the changed surface of the membrane and hence its changed adsorbing power. All the non aqueous solvents seemed to have a hardening, stiffening effect upon the paper making it very easy to handle without changing its texture, but water left the papers very soft and easily broken. Also when pressed to remove the air those in water must have changed materially. It has been shown by Bancroft[112] that the surface condition largely determines the adsorbing power of any solid medium.

If the endosmose is directly proportional to the applied voltage, as the equation asserts, then the curves of endosmose against voltage should be straight lines. Briggs[113] found in water a slight excessive increase at high voltage, but he only worked up to 530 volts. Curves (Tables 42-50) show that, with both water and non aqueous solutions, this increase becomes even greater at higher voltages. It becomes so great in fact that the curve can no longer be regarded as a straight line. This may be partially explained by electrolysis effects at high voltage and partially by the decrease shown in the continuous run experiments listed in Tables 2 to 8. However, this does not change the fact that the curve is not a straight line and that through wide ranges of voltage, as here measured, the endosmotic flow is not a linear function of the applied voltage.

The acid-alkali curves (Tables 51-56) show the same maximum as the concentration curves at about the same concentra-

112. Loc. cit.

113. Loc. cit.

tion of solution. In water solutions acid generally gives negative endosmose, unless extremely dilute, and alkalies give positive endosmose due to the adsorption respectively of the H and OH ions. This was not true in every case with non aqueous solutions and in some cases the increased concentration increased the flow to the cathode. (Tables 51, 52, 55, 56). The alkali increased the cathode flow in every case except for the stated maximum. This discrepancy with the acid can only be explained by a chemical reaction between the acid used and the solvent, or a difference in adsorption in non aqueous media of the H ion. Chemical action might produce an ion or a molecule less effective or opposite in its effects to that of the H ion.

The curves of endosmose against temperature (Tables 57-63) show that, as Briggs[114] has stated, the endosmose is not directly proportional to the fluidity but increases slightly less rapidly. Cruse[115] thought that there was a maximum endosmose at a definite temperature, but no evidence of such was obtained, except in the case of acetone where the decrease was clearly due to the formation of bubbles in the membrane and measuring tube.

Probably the effect of the addition of certain salts has been the hardest to explain. This effect was noted in Tables 64-77. As solution was often very difficult, ⠀ the results were doubtless in many cases purely molecular. Further, this molecular effect might be one of solvation, an effect which

114. Loc. cit.

115. Phys. Zeitschr., 6, 201 (1905).

with our present knowledge is impossible to predict. Most of the results in these tables can be explained on the theory of selective adsorption but, if so, another assumption must follow as a logical conclusion. That is: the amount of adsorption and the relative adsorption varies with the medium in which the salt is dissolved. The order of adsorption of ions has been carefully worked out in water[116] but the results given here show it is not the same in other solvents. Table 64 shows Al less adsorbed than Ca and Table 68 the reverse. Table 72 shows Na, ordinarily only slightly adsorbed, having a greater effect than Ca. In fact, the tables are full of such apparent irregularities. The effect might be due to a chemical reaction between the salt and the organic substance. This would doubtless explain several instances, the new substance formed producing a highly adsorbed ion which determines the direction and amount of endosmotic flow. All attempts to apply a valency rule similar to that with water, that the effect increases with increasing valence, were unsuccessful, except in one or two cases cited in the earlier discussion of this same topic. Nor was there found to exist any such relationship as that suggested by Holmes,[117] that the endosmose varies as the velocity of the cation divided by the valence. The conditions in organic solvents are certainly different from those in water.

When the concentration was changed the results shown in Tables 78-84 are obtained. This same type of curve was noted in the acid alkali runs. This maximum in the curve is produced by the

116. Hofmeister Series.

117. Loc. cit.

fact that at high concentrations, much more evident here than with water, the salt is doubtless largely in a molecular condition. As the substance is diluted, ions are produced in larger quantities, which being preferentially adsorbed tend to increase the effects. Now, when the solution was diluted further and the ions became less numerous, less of this adsorption effect was evident and more of the effect produced by the pure solvent in contact with the membrane. This would account for the reversal through zero of the curves: Tables 78, 82, 83. This maximum seemed to come at about the same concentration, N/10000, in each case showing that these salts at least were probably completely dissociated at this dilution. Should further study show that this maximum varies, it would indicate the necessity of comparing salt solutions, not of the same concentration but of maximum flow regardless of the concentration. Barratt and Harris[118] and Loeb[119] more recently have noted this same maximum condition in endosmose and the latter in "free osmosis". It should be recalled again that the adsorption, concentration curve is parabolic, which would also assist in producing this type of curve, for as the concentration of the salt increases, its adsorption increases to a maximum, thus producing this maximum effect which might or might not coincide with the effect just discussed.

The curves for Tables 85-92 illustrate the effect of adding water to the solvent. The equation shows endosmose inversely proportional to the viscosity coefficient. Acetone has a much lower

118. Loc. cit.

119. Loc. cit.

viscosity than water; so low that it manifested little friction in the measuring tube and membrane. This would partially explain the curve for Table 85. Further, acetone and water are not equally adsorbed and each would tend to have its own effect and, as that of water is the greater, a small amount would cause at first a large change in endosmose rate. However, after a salt is added the relative adsorption of the ions must also be considered. The NO_3 ions are adsorbed most in the water and hence, above a certain concentration, the curve showed a decided increase of endosmose rate. But in the acetone the Na is more highly adsorbed as shown in the run on dissolved salts (Tables 64 and 66). These factors work against each other and account for the nature of the curve in this case.

In the curves for amyl alcohol and also for n-butyl alcohol the effect is probably largely due to changes taking place at the membrane. In this case the alcohols produce a positive charge on the membrane and water a negative charge. When water is added, it, being much more highly adsorbed, manifests its effects and causes reversal of flow at a very low concentration. When the salt is added the results are the same and hence the NO_3 ion is preferentially adsorbed in both media.

With pyridine (Table 89), as the viscosity decreased and the adsorption of water increased, the rate gradually increased. In Table 90 the conditions of amyl alcohol were repeated, except that here, as the membrane in pyridine was originally charged negatively, the K ion of KCNS must have been most highly adsorbed; while in water it was the CNS ion. This caused the reversal and passage through zero when water was added.

The equation given indicates the endosmose as directly proportional to the dielectric constant. This is quite well shown in Table 93 and the previous runs on the solvents studied. The dielectric constant for water is given as about 80;[120] amyl alcohol as 10-30; acetone, 20.7-33.8; nitrobenzene, 34-42; pyridine, 12.4; benzaldehyde, 14-17; and n-butyl alcohol as 18. While nitrobenzene should then give a greater endosmose than acetone, it does not because of its greater viscosity and lower adsorptive factor. In every case of orgahic solvents the membrane remained firm and hard in the solvent. while in water, and to a less extent in pyridine, it became soft and difficult to handle. Further, some of the substances had a much less affinity for the glass, a factor not due to viscosity or proportional to it, and thus an additional factor in affecting the flow through the bubble tube. All of these must be taken into account in comparing dielectric constant effects as they are factors not duplicable. If this dielectric constant ratio is determined by an adsorption effect it must largely depend upon the nature of the membrane surface.

If endosmotic flow is determined by the adsorption and consequent orientation of the solvent molecules, largely affected by the adsorption of substances present in solution, we must consider the total effect as due to all these adsorbed substances. Both of the ions of a substance must be adsorbed in varying amounts and each must have its effect. When the potential difference is applied the movable liquid will be directed through by the contact

120. Landolt, Börnstein.

charge, the cation adsorbed and the anion adsorbed. The true flow
then will be the algebraic sum of such flow in both directions as
determined by the relative adsorption of the particular ions and
the interfacial charge of the membrane and solution, other factors
being equal.

In all probability the apparatus used in these experiments,
because the current was reversed every few seconds, would eliminate
ion mobility effects. But in the light of Bartell's[121] and Loeb's[122]
work on "free osmosis" there must be some relationship existing.
Ions moving at different rates are bound to produce in the capil-
laries an orientation of charges on opposite ends of the pores,
and though this would be reversed with the current, it must during
the small interval of time have an effect upon the endosmotic flow.

There is present in most papers on electric endosmose
some reference to solvation effects. The recent work by Remy[123]
has made it seem even more plausible. As the solution moves more
or less rapidly through the membrane, the ions are at the same time
moving toward the electrodes, and the question as to whether or
not such ions are solvated becomes one of important consideration.
This is directly connected with the transport rate of the ions,
the slower ions being more solvated and carrying a greater amount
of solvent than the more rapid ones. This effect would also tend
to be neutralized by the reversal of current but must manifest its
small effect during the run. Such a solvation effect might even be

121. Loc. cit.

122. Loc. cit.

123. Loc. cit.

used to explain some of the curves.   If the ion is slightly sol-
vated and the molecules highly so, then an increase in concentra-
tion would first decrease and then increase the flow. This problem
will be studied further using Remy's method.

SUMMARY AND CONCLUSIONS FOR PART I

In this paper the author has given a comprehensive
review of all the previous work pertaining to electric endosmose.

Experiments measuring endosmotic flow have been conducted
with water and six typical organic solvents, using a modified
Briggs' "osmometer" which has been described in detail.

A source of high voltage available for non aqueous
solvents has been described.

A more comprehensive theory for the production of the
contact charge has been proposed.

The following conclusions were reached.

1. The permeability of the membrane is an important
factor in determining endosmotic effects.

2. It is possible to duplicate membranes of filter
paper when using non aqueous solvents.

3. The endosmose rate is not a linear function of the
applied voltage when considered over a wide range but increases
re rapidly than the voltage.

4. The effect of acid and alkali can be explained on
the assumption of adsorption, making due allowance for concen-
tration and the possibility of chemical change.

5. Briggs' results as to temperature effect with water have been confirmed with non aqueous solvents.

6. The valence rule does not hold with the non aqueous solutions studied but this may be partially due to chemical action.

7. The order of adsorption of ions and their relative adsorption varies with the solvent.

8. The concentration curve exhibits a maximum with non aqueous solutions at about N/10000 and at low concentrations the flow is in the same direction as that of the pure solvent.

9. The addition of water to non aqueous solutions changes the endosmose in the direction it would manifest with pure water, the first additions showing the greatest effects.

10. The direction of endosmose is not determined by the dielectric constant ratio though this probably does measure the magnitude of flow.

This work is being continued with a greater variety of organic solvents.

ELECTRIC ENDOSMOSE Part II.

Further studies on non aqueous solvents.

An adsorption orientation theory.

Some mathematical conceptions.

Acknowledgement

Additional credit is due Professor H. W. March,
who assisted the author in the mathematical con-
ceptions presented in this part of the paper.

INTRODUCTION

In Part I of this paper there has been presented a long list of experimental data on phenomena directly affecting the rate of electric endosmose flow. This work was carried out with organic solvents. Although some of the conclusions were the same as for water, many were in direct variance with those of former investigators. A new theory for the development of the contact potential was suggested. It is the purpose of this section of the paper to present additional evidence for the former statements, using three more non aqueous solvents. Also to draw inferences from a new series of runs using the anions and cations of the Hof meister series and to present a discussion of the more firmly established adsorption, orientation theory, considered from the standpoint of the thermodynamic and electrostatic environment at the surface of contact of the solvent and membrane. Some mathematical conceptions which have grown out of these experiments are also presented.

APPARATUS

The apparatus used was the same as that employed in the previous work. The battery system had been standing unused since the early part of July. The total available e. m. f. had dropped from 954.0 volts to 929.0 volts by Sept. 27th. On Oct. 12th this had fallen to 920 volts. Only in two cases had the batteries shown signs of deterioration. This was doubtless caused by moisture being absorbed through small openings in the sealing wax cover due to too high temperature when soldering.

PREPARATION OF MATERIALS

Three new solvents were used in this work: furfural, isopropyl alcohol, and o-nitrotoluene.

The furfural was Eastman's product No. 140. It was quite dark when it was received but became a light yellow upon distillation. It rapidly darkened to the original color upon exposure to the air during the run. Its boiling point was 161.8°.

The isopropyl alcohol was Eastman's product No. 212. It contained a slight trace of water and was redistilled after standing over anhydrous $CuSO_4$ for several days. Its boiling point was 81.5° - 82.5°.

The o-nitro toluene was Eastman's product No. 193. It was redistilled and had a boiling point of 217.6° - 218.0°.

The succinic acid, sodium hydroxide and salts used for cation and anion effect were the same samples formerly purified. The salts used for the "Hofmeister Series" runs were the purest obtainable and were merely dried and kept in weighing bottles in a desiccator. The same grade of filter paper (Schleicher and Schüll No. 589) was used.

To make these results easily comparable with the former, the same order is employed in their presentation.

EXPERIMENTAL

A long continuous run was made with each solvent to determine the number of runs necessary for an average effect. These results are shown in Table 1 and its accompanying curve for furfural; Table 2 for isopropyl alcohol; and Table 3 for o-nitro-toluene.

TABLE 1

Sept. 29, '20.

Voltage 750.0   Current 1.0   Temp. 25°   Bubble 4 m.m.

Solution - furfural   Membrane (6 Thickness S&S No. 589)

Osmose + sec for 10 cm.

L	1	2	3	4	5	R	1	2	3	4	5
	55.0	54.0	50.5	51.0	50.2		55.0	54.0	53.2	52.5	51.8
	6	7	8	9	10		6	7	8	9	10
	50.2	49.0	49.0	49.0	49.8		52.0	51.0	50.4	50.8	51.0
	11	12	13	14	15		11	12	13	14	15
	49.6	50.0	49.5	49.0	49.4		50.0	50.5	50.0	50.0	50.0
	16	17	18	19	20		16	17	18	19	20
	49.0	48.5	46.5	47.0	46.0		50.0	49.5	48.5	48.0	48.5

TABLE 2

Oct. 6, '20.

Voltage - 859.0   Current 1.0 +   Temp. 25°   Bubble 5 m.m.

Solution - isopropyl alcohol   Membrane (4 Thickness S&S-No. 589)

Osmose + sec for 10 cm.

L	1	2	3	4	5	R	1	2	3	4	5
	14.5	13.0	13.2	13.5	14.0		13.0	12.5	12.0	12.5	12.5
	6	7	8	9	10		6	7	8	9	10
	14.0	15.0	15.0	15.8	16.0		13.0	13.2	13.2	13.0	14.5
	11	12	13	14	15		11	12	13	14	15
	16.2	16.5	16.5	16.5	15.8		14.5	15.0	15.0	15.0	15.5
	16	17	18	19	20		16	17	18	19	20
	16.5	17.0	17.0	17.2	17.2		16.0	15.6	16.0	16.0	17.0

TABLE 3

Oct. 13, '20.

Voltage 850.0   Current 0   Temp. 25°   Bubble 5.5 m.m.

Solution - o-nitrotoluene   Membrane (6 Thickness S&S No. 589)

Osmose + sec for 10 cm.

L	1	2	3	4	5	R	1	2	3	4	5
	23.0	23.0	22.0	21.4	19.8		23.0	22.5	21.8	20.0	19.0
	6	7	8	9	10		6	7	8	9	10
	19.0	18.0	17.6	17.4	17.0		18.0	17.8	17.4	17.0	17.0
	11	12	13	14	15		11	12	13	14	15
	16.2	16.0	15.5	15.0	15.5		16.6	16.5	15.8	15.8	16.0
	16	17	18	19	20		16	17	18	19	20
	15.5	15.0	15.0	14.8	14.4		15.5	15.5	15.5	15.0	15.4

For Table 1.

For Table 2.

No. of run.

For Table 3.

No. of Run.

t. Sec. for 10 cm.
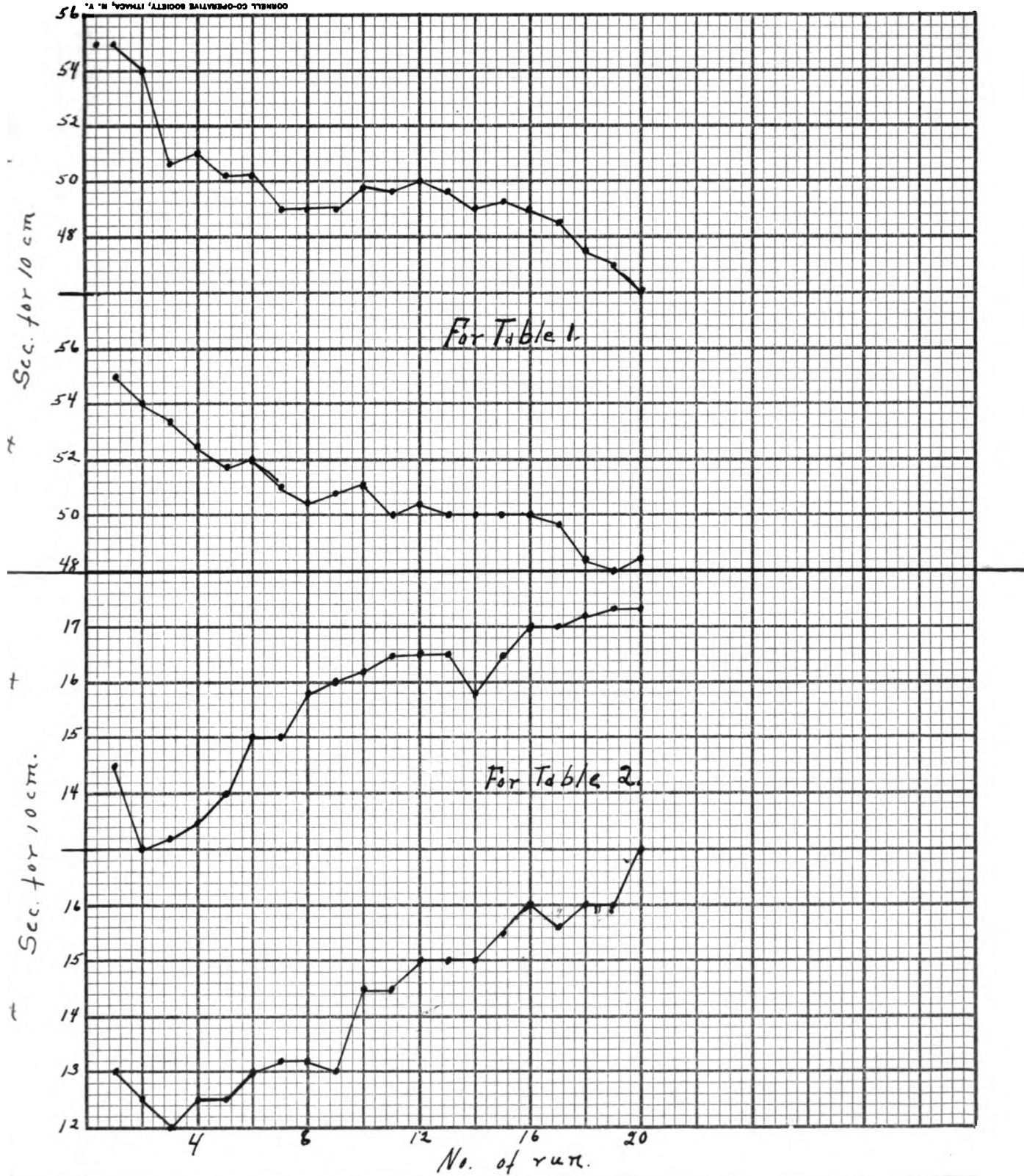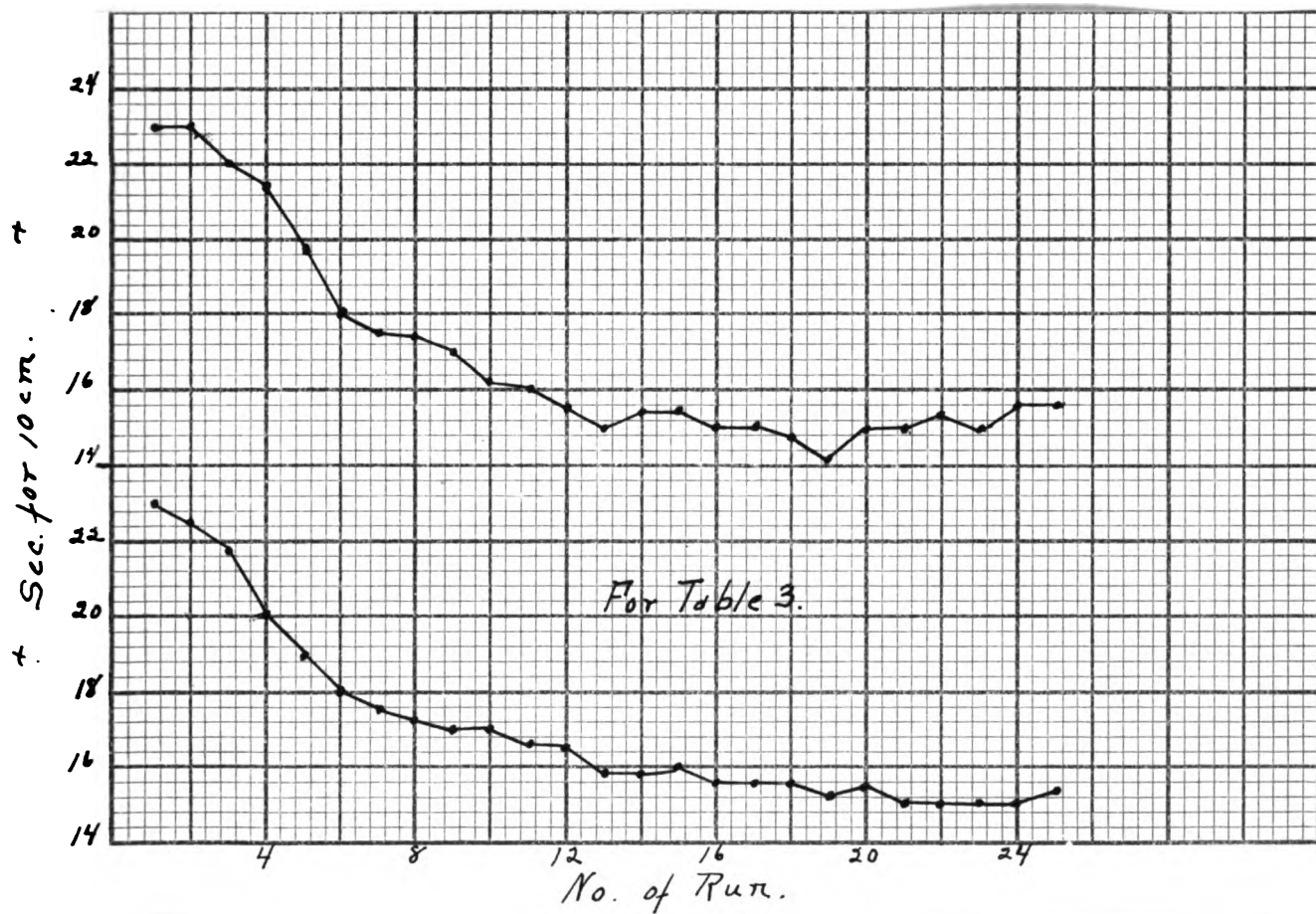
Isopropyl alcohol reached a maximum rate very quickly
so that it was only necessary to average the first few runs. The
maximum with o-nitrotoluene came at about the twentieth run
while furfural seemed to gain continually. This continuous
increase with furfural was doubtless due to oxidation and
electrolysis effects. The substance is very much like benzal-
dehyde in its properties though the latter reached a maximum
after but a very few runs. These curves served as a criterion
for the number of runs necessary to obtain an average rate.

EFFECT OF CHANGE OF PERMEABILITY

The permeability of the membrane was changed by varying
the thickness. The results obtained by plotting rate of endosmose
against rate of permeability, for a particular membrane, are shown
in curves; Table 4 for furfural, Table 5 for isopropyl alcohol,
and Table 6 for o-nitrotoluene.

TABLE 4

Sept. 28, '20.

Furfural vs SMS Paper No. 589.

Membrane Thickness	Solution Furfural	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
2	"	750.0	3.0	+	25°	6 m.m.	0.195	26.0×10^{-5}	2.08
4	"	"	"	+	"	5 " "	0.198	26.4 x "	1.15
8	"	"	"	+	"	4.5" "	0.200	26.6 x "	0.67
12	"	"	"	+	"	3 " "	0.208	27.7 x "	0.53
16	"	"	"	+	"	5.5" "	0.194	25.8 x "	0.34

TABLE 5

Oct. 5, '20.

Isopropyl Alcohol vs SMS Paper No. 589

Membrane Thickness	Solution Isopropyl	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
2	Alcohol	859.0	1.0-	+	25°	6 m.m.	0.348	40.5×10^{-5}	0.83
4	"	"	"	+	"	4.5" "	0.569	66.2 x "	0.50
6	"	"	"	+	"	6 " "	0.540	62.8 x "	0.42
8	"	"	"	+	"	7 " "	0.352	59.6 x "	0.53
12	"	"	"	+	"	4 " "	0.342	39.8 x "	0.26
1	"	"	"	+	"	7 " "	0.299	34.8 x "	1.50

TABLE 6

Oct. 13, '20.

O-Nitrotoluene vs S&S Paper No. 589

Membrane Thickness	Solution O-Nitrotoluene	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
2	"	850.0	0	+	25^0	4 m.m.	0.464	54.5×10^{-5}	2.58
4	"	"	0	+	"	6 " "	0.529	62.2 x "	1.30
6	"	"	0	+	"	5 " "	0.654	76.9 x "	0.70
8	"	"	0	+	"	5 " "	0.353	41.5 x "	0.52
12	"	"	0	+	"	5 " "	0.297	34.9 x "	0.44
1	"	"	0	+	"	4 " "	0.262	30.8 x "	5.00

For Table 4.

Rate of Osmose

For Table 5.

Rate of Osmose.

For Table 6.

Rate of Osmose.
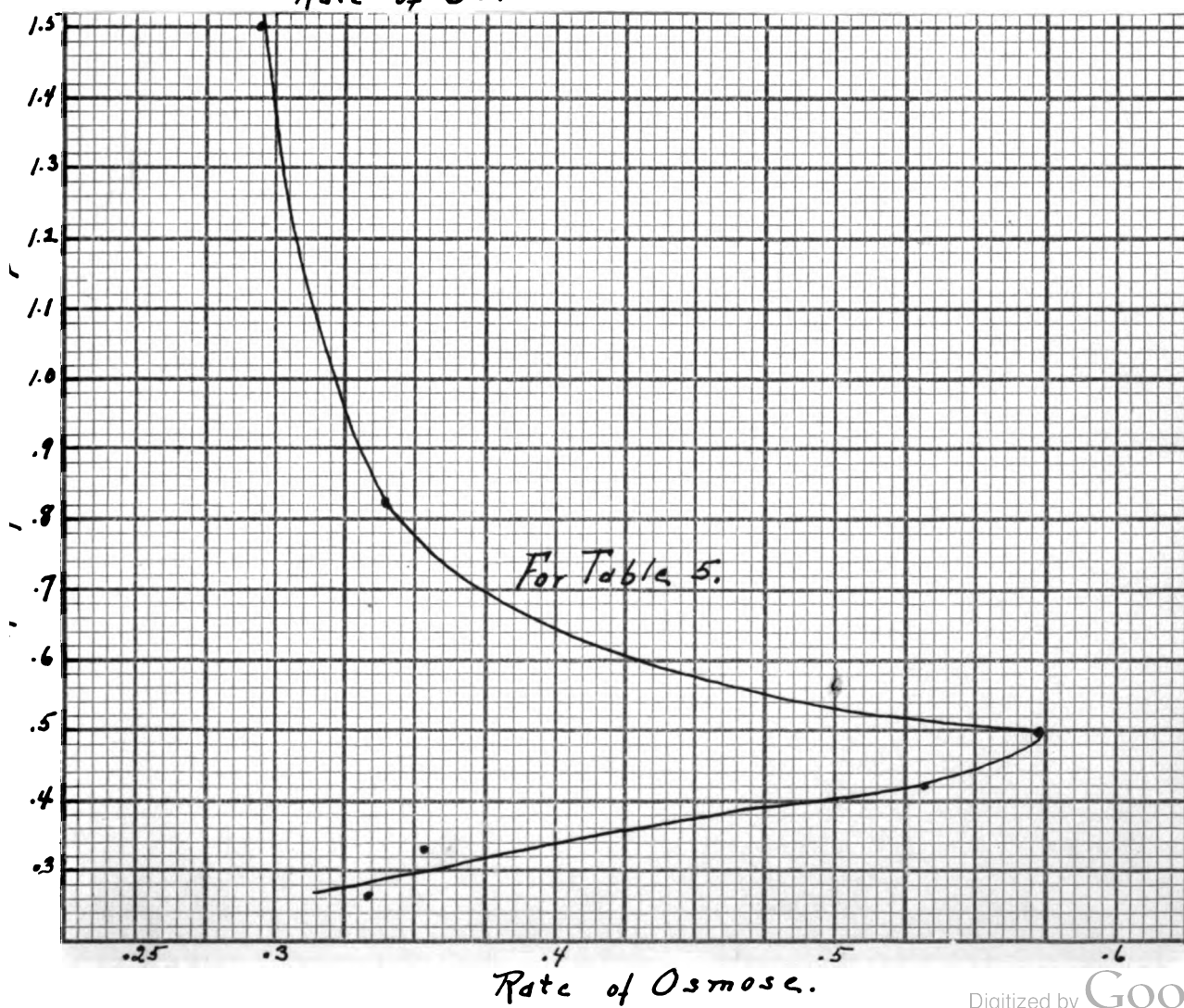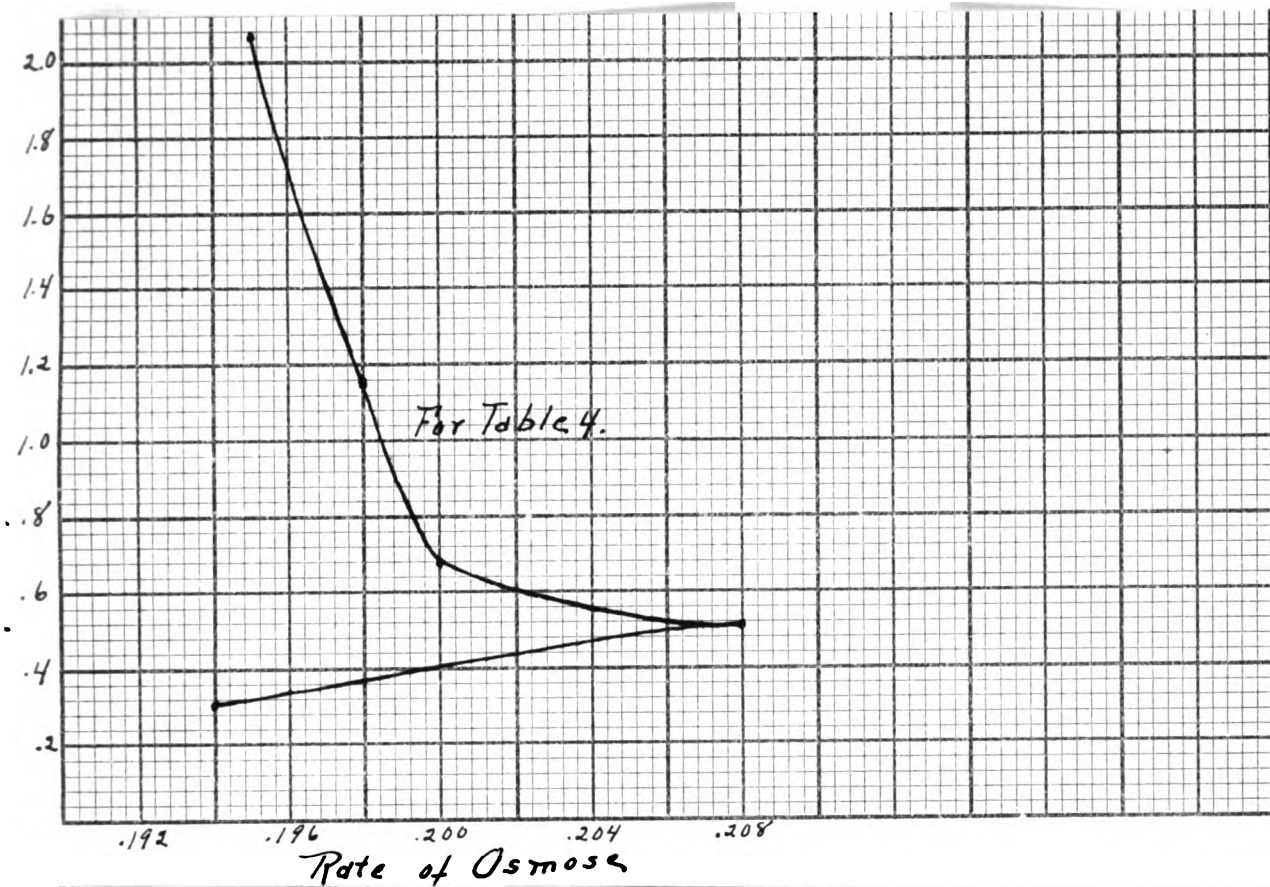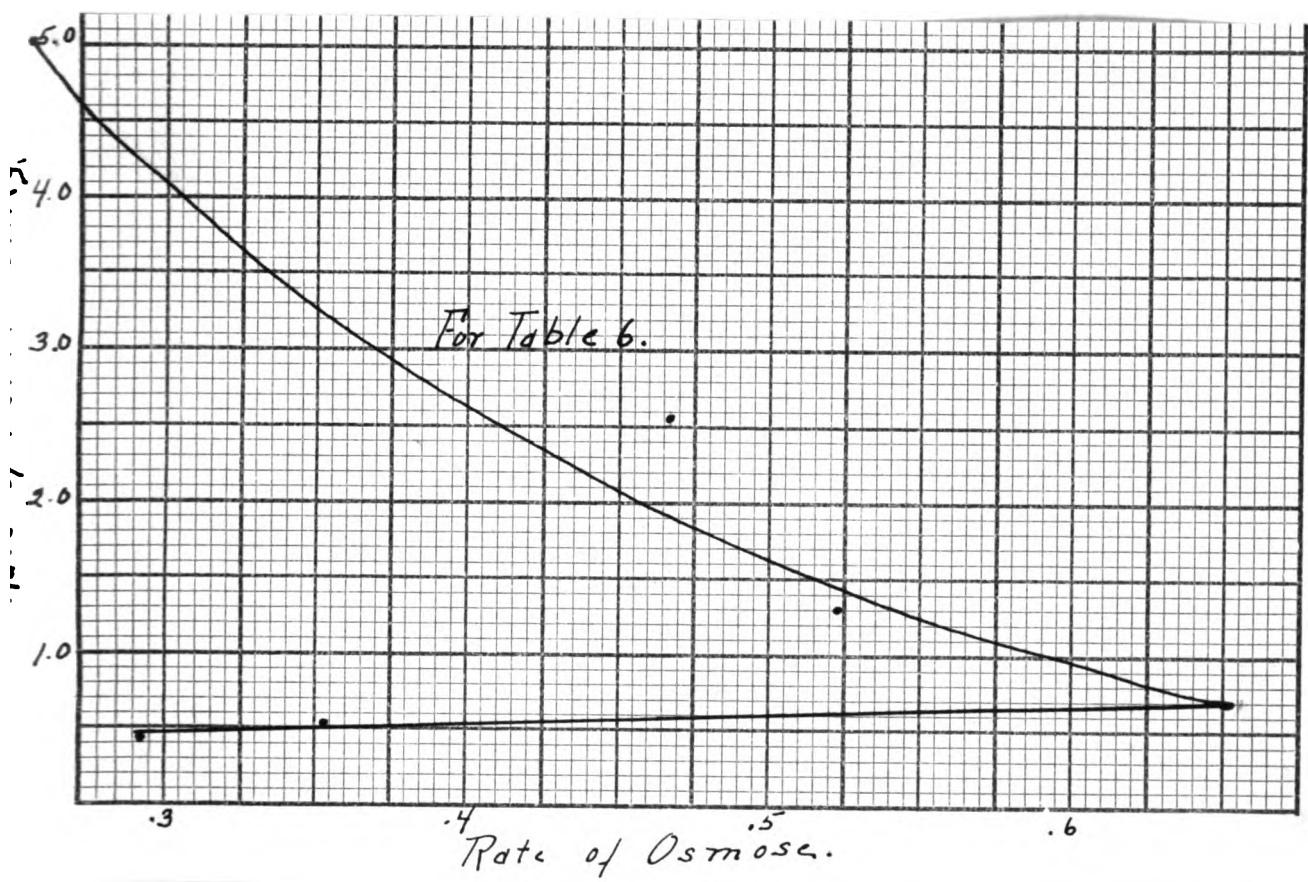
We have exactly the same type of curves as in the previous work. So striking a regularity cannot be mere coincidence. A mathematical discussion will be presented for these curves.

DUPLICATION

Duplication runs were also made on these solvents, keeping all factors as nearly constant as possible. These showed about the same degree of regularity as did the previous six solvents. The variation may be partly due to differences in permeability but largely to a slight difference in the environment at the surface of opntact of the membrane and solvent. Table 7 gives the results using furfural, Table 8 for isopropyl alcohol, and Table 9 for e-nitrotoluene.

TABLE 7

Sept. 28, '20.

Furfural vs S&S Paper No. 589.

Membrane Thickness	Solution Furfural	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
6	"	750.0	1.0	+	25°	5 m.m.	0.201	26.8 x 10^{-5}	0.83
6	"	"	1.0	+	"	3 " "	0.202	26.9 x "	0.87
6	"	"	1.0	+	"	5 " "	0.204	27.2 x "	1.00
6	"	"	1.0	+	"	4 " "	0.204	27.2 x "	1.03

TABLE 8

Oct. 6, '20.

Isopropyl Alcohol vs S&S Paper No. 589

Membrane Thickness	Solution Isopropyl Alcohol	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
4	"	859.0	1.0+	+	25°	5.5m.m.	0.630	73.3 x 10^{-5}	0.55
4	"	"	1.0+	+	"	5.5" "	0.707	82.2 x "	0.50
4	"	"	1.0+	+	"	5 " "	0.717	83.4 x "	0.60
4	"	"	1.0+	+	"	5 " "	0.720	83.8 x "	0.71

TABLE 9

Oct. 13, '20.

O-Nitro Toluene vs S&S Paper No. 589

Membrane Thickness	Solution O-Nitro toluene	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
6	"	850.0	, 0	+	25°	4 m.m.	0.660	77.6 x 10^{-5}	0.85
6	"	"	0	+	"	6 " "	0.654	76.9 x "	0.89
6	"	"	0	+	"	5 " "	0.649	76.3 x "	0.90
6	"	"	0	+ ,	"	5.5" "	0.655	77.7 x "	0.88

For Table 10.

Rate of Osmose.

For Table 11.

Rate of Osmose.

For Table 12.
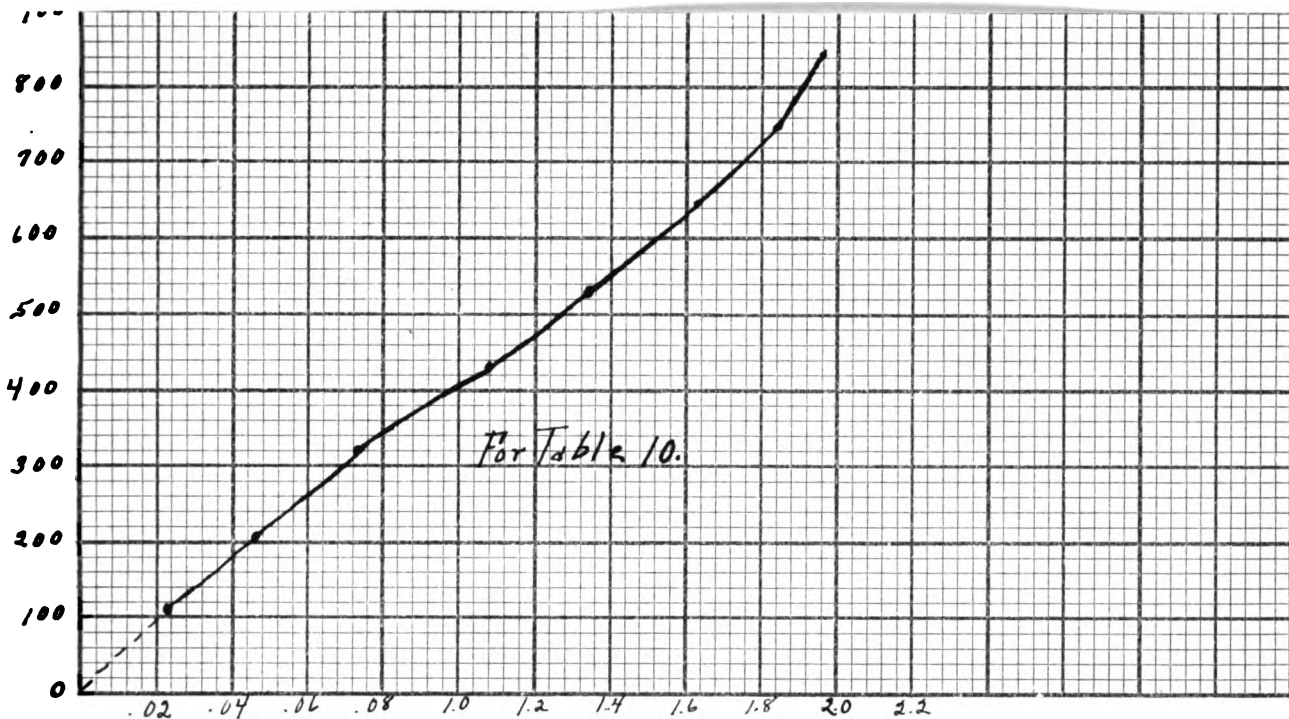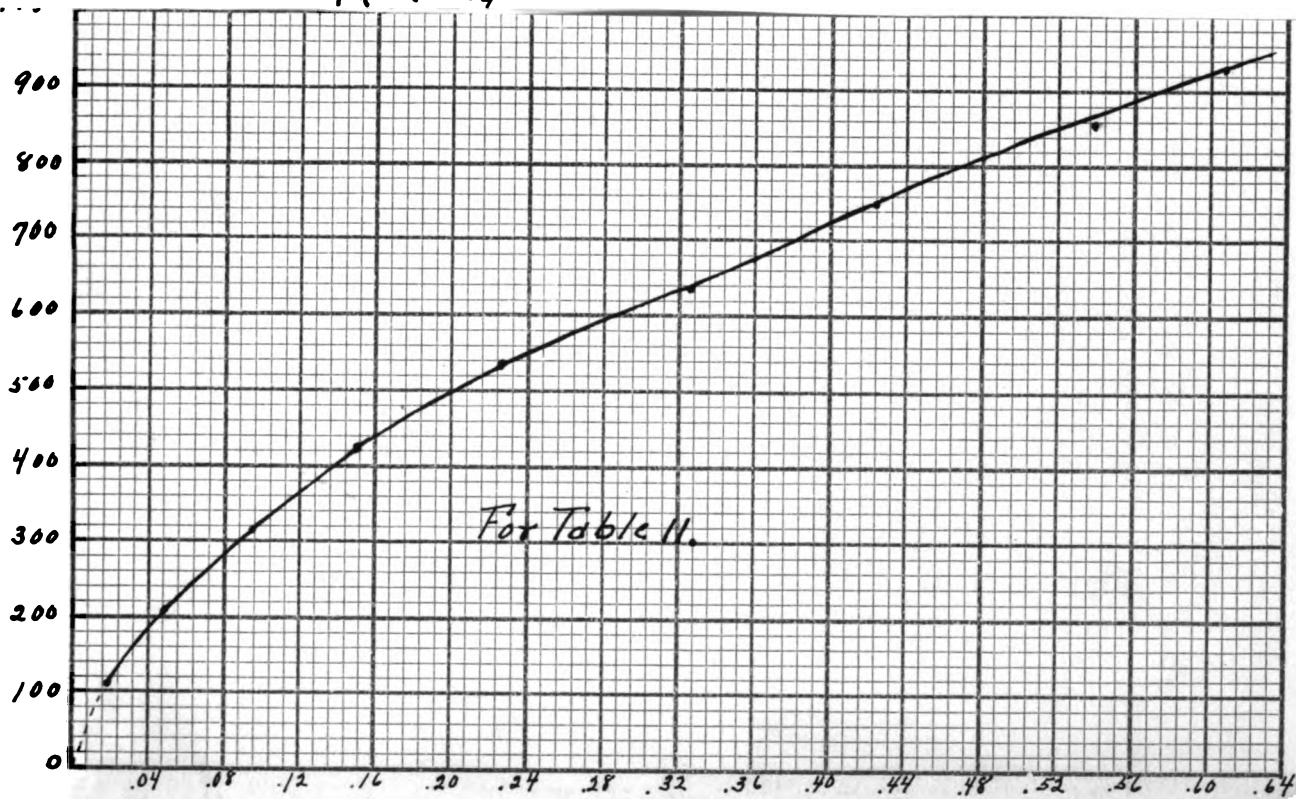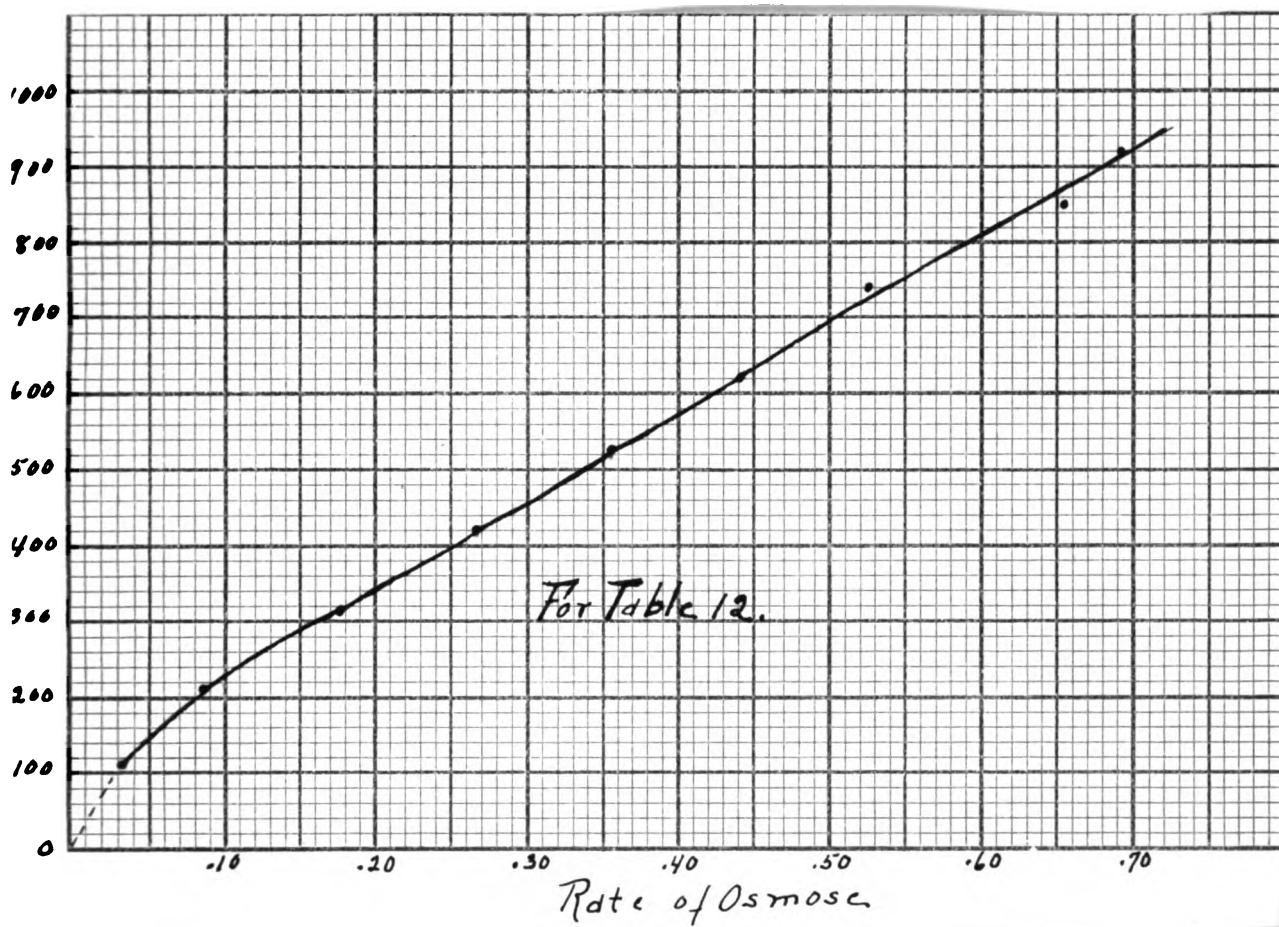
Rate of Osmose

EFFECT OF VARYING THE APPLIED POTENTIAL

In the previous work it was not possible to secure a
linear function relationship between applied potential and rate
of endosmose. Thinking this might be due to a falling off of
the electromotive force of the batteries, readings were taken
only after a careful checking up of the system. This was repeated
several times during the run and at the end, but showed no
measurable variation. The results obtained from readings taken on
a single membrane and solvent were quite comparable with the ear-
lier studies. Table 10 and its curve are for furfural, Table 11
for isopropyl alcohol, and Table 12 for o-nitro toluene. Both
isopropyl alcohol and o-nitro toluene exhibited a slight piling
up when applying high voltages. There will be presented a
mathematical correction to the equation for electric endosmose
which represents this variation from a linear function.

TABLE 10

Sept. 28, '20.

Furfural   Permeability = 1.00 cm/sec

Run No.	Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
	6 Thickness	Furfural							
1	S&S-589	"	859.0	5.5	+	25°	5 m.m.	0.198	23.0 x 10^{-5}
2	"	"	750.0	5.0	+	"	"	0.182	24.2 x "
3	"	"	640.0	4.0	+	"	"	0.161	25.1 x "
4	"	"	534.0	3.5	+	"	"	0.136	25.4 x "
5	"	"	425.0	3.0	+	"	"	0.107	25.1 x "
6	"	"	318.0	2.5	+	"	"	0.077	24.2 x "
7	"	"	210.0	1.5	+	"	"	0.048	22.8 x "
8	"	"	104.0	1.0	+	"	"	0.022	21.1 x "

TABLE 11

Oct. 5, '20.

Isopropyl Alcohol   Permeability = 0.42 cm/sec

Run No.	Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
	6 Thickness	Isopropyl Alcohol							
1	S&S-589	"	929.0	1.5	+	25°	6 m.m.	0.609	65.5 x 10^{-5}
2	"	"	859.0	1.0	+	"	"	0.540	62.8 x "
3	"	"	750.0	1.0	+	"	"	0.424	56.5 x "
4	"	"	640.0	1.0	+	"	"	0.324	50.6 x "
5	"	"	534.0	0.5	+	"	"	0.234	43.8 x "
6	"	"	425.0	0.5	+	"	"	0.156	36.7 x "
7	"	"	318.0	0+	+	"	"	0.096	30.1 x "
8	"	"	210.0	0	+	"	"	0.054	25.7 x "
9	"	"	104.0	0	+	"	"		

TABLE 12

Oct. 12, '20.

O-Nitro Toluene   Permeability = 0.70 cm/sec

Run No.	Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
6	Thickness	O-Nitro Toluene							
1	S&S-589	"	920.0	0	+	25°	5 m.m.	0.693	75.2 x 10^{-5}
2	"	"	850.0	0	+	"	"	0.654	76.9 x "
3	"	"	742.0	0	+	"	"	0.534	71.9 x "
4	"	"	632.0	0	+	"	"	0.446	70.5 x "
5	"	"	525.0	0	+	"	"	0.352	67.0 x "
6	"	"	418.0	0	+	"	"	0.263	62.4 x "
7	"	"	315.0	0	+	"	"	0.171	54.2 x "
8	".	"	207.0	0	+	"	"	0.090	43.4 x "
9	"	"	104.0	0	+	"	"	0.040	38.4 x "

For Table 13.

Rate of Osmose

For Table 14.

Rate of Osmose

For Table 15.

Rate of Osmose.
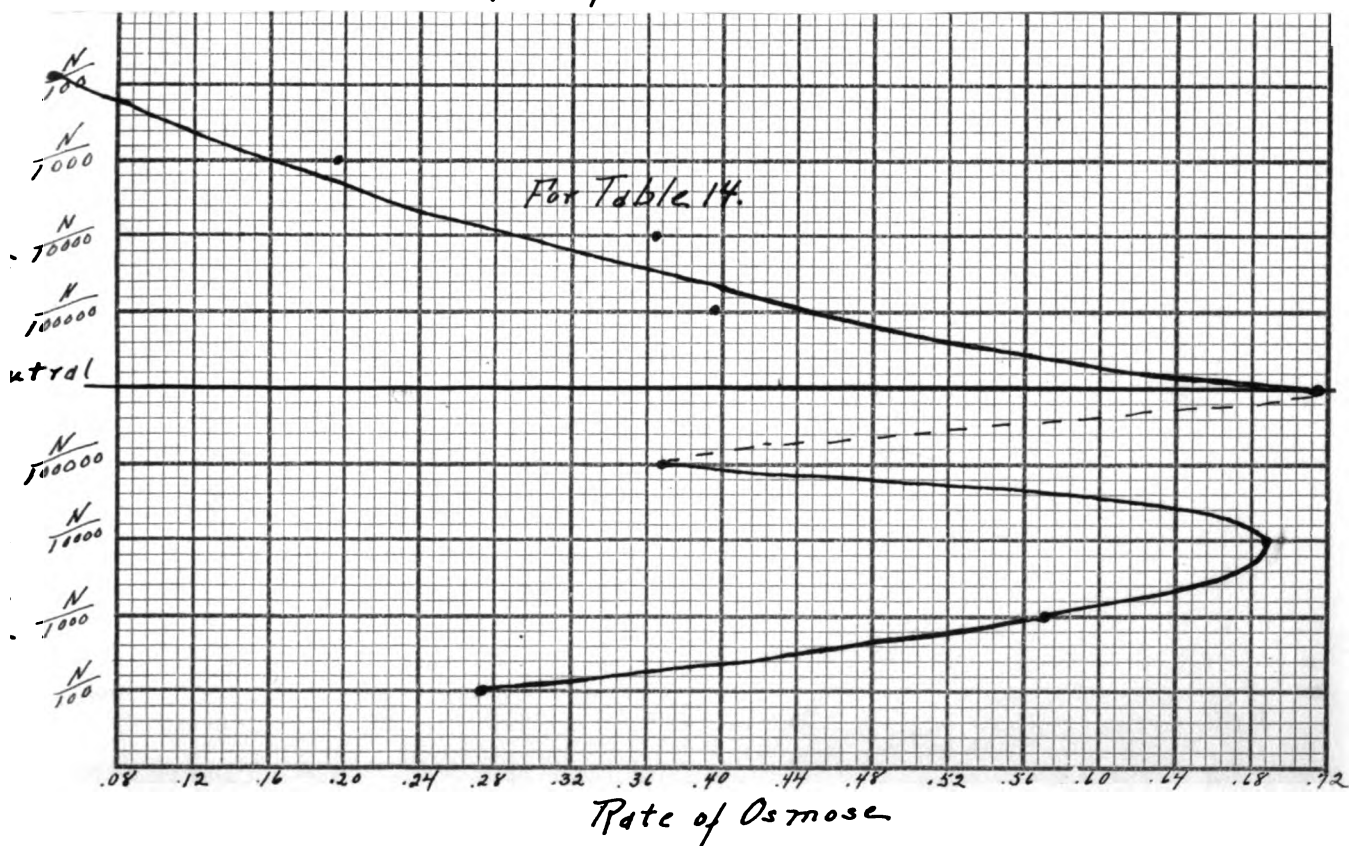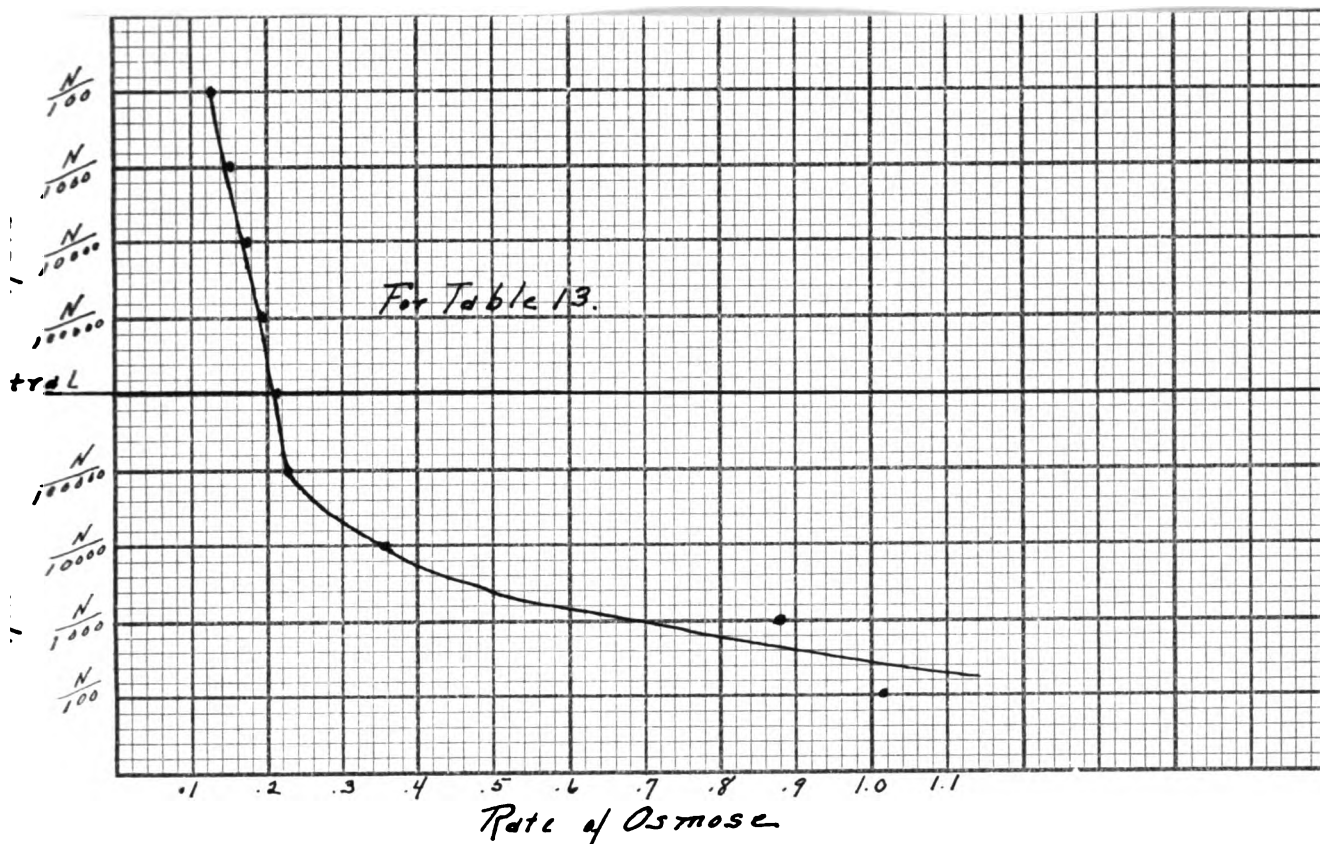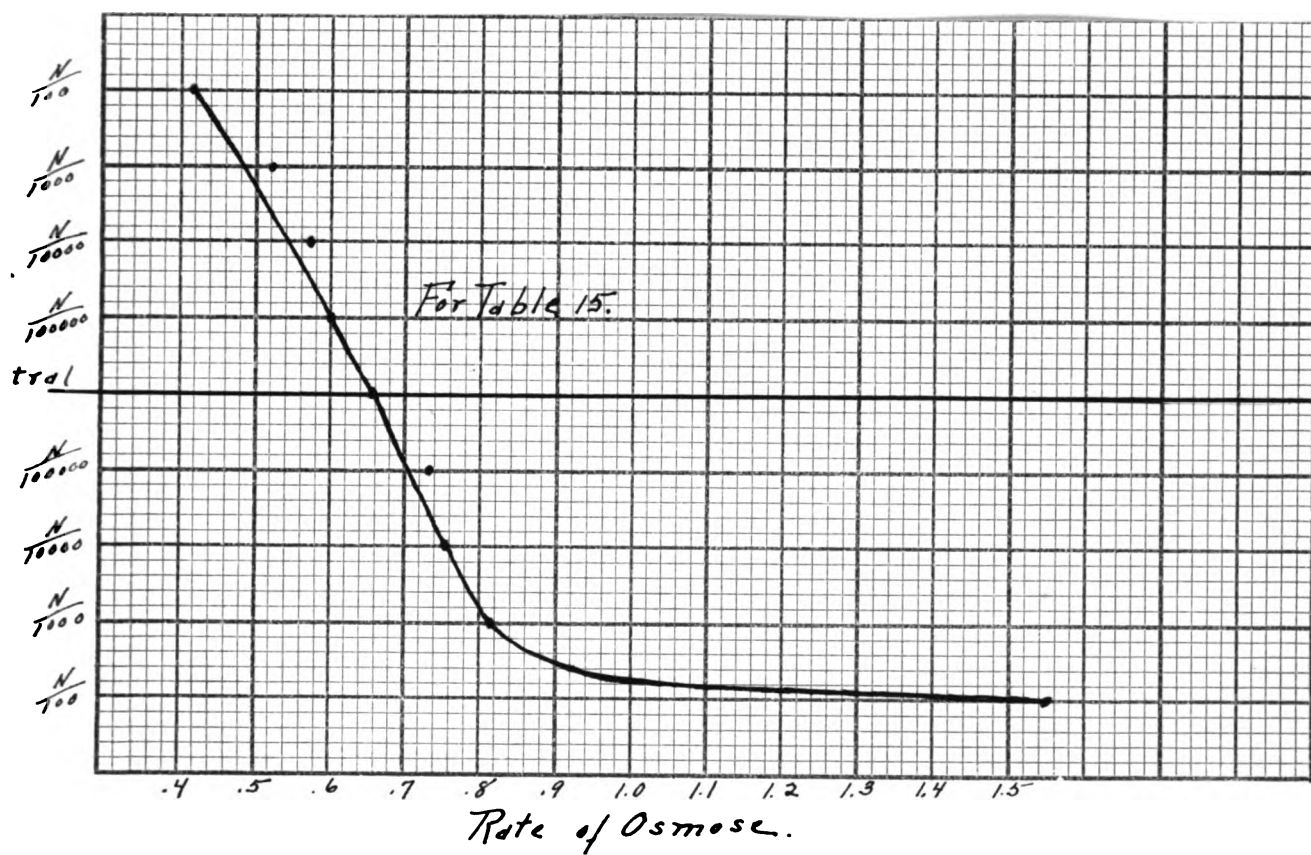
THE EFFECT OF THE ADDITION OF ACID AND ALKALI

As before, succinic acid and sodium hydroxide were used for these tests. The concentration was varied from N/100 to N/100000. The curves for furfural (Table 13) and for o-nitro toluene (Table 15) are perfectly regular. In both cases the acid caused a gradual decrease in rate and the alkali an increase, as might be expected from selective adsorption of the H and OH ions. The curve for isopropyl alcohol (Table 14) exhibits some peculiar changes very likely due to chemical action. Furthermore, this was the only solvent which showed the maximum peculiar to a change of concentration. This maximum came at about N/1000.

TABLE 13

Sept. 30, '20.

FURFURAL

Membrane Thickness	Solution Succinic	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
k3-589	N/100000	750.0	2.0	+	25°	5 m.m.	0.183	24.4 x 10^{-5}	1.09
"	N/10000"	"	2.0	+	"	5.5" "	0.181	24.1 x "	1.03
"	N/1000 "	"	2.0	+	"	7 " "	0.169	22.5 x "	1.15
"	N/100 "	"	2.0	+	"	6.5" "	0.133	17.7 x "	1.03
"	Neutral NaOH	"	1.0	+	"	5 " "	0.201	26.8 x "	0.83
"	N/100000*	"	2.0	+	"	7 " "	0.202	26.9 x "	0.93
"	N/10000 "	"	3.0	+	"	4.5" "	0.360	48.0 x "	1.05
"	N/1000 "	"	6.5	+	"	4.5" "	0.871	116.1 x "	1.11
"	N/100 "	"	13.0	+	"	4 " "	1.029	137.2 x "	1.00

TABLE 14

Oct. 6, '20.

ISOPROPYL ALCOHOL

Membrane Thickness	Solution Sucocinic	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	N/100000 "	859.0	1.5	+	25°	5.5m.m.	0.394	45.8×10^{-5}	0.51
"	N/10000 "	"	"	2.0	+	"	5.5" "	0.361	42.0 x "	0.52
"	N/1000 "	"	"	2.0	+	"	7 " "	0.199	23.1 x "	0.50
"	N/100 "	"	"	2.5	+	"	4 " "	0.041	4.7 x "	0.57
"	Neutral NaOH	"	1.0	+	"	5 " "	0.717	83.4 x "	0.60
"	N/100000 "	"	1.5	+	"	6 " "	0.370	43.0 x "	0.55
"	N/10000 "	"	"	2.0	+	"	5.5" "	0.689	80.2 x "	0.50
"	N/1000 "	"	"	6.5	+	"	6.5" "	0.568	66.1 x "	0.57
"	N/100 "	"	"	43.0	+	"	5 " "	0.276	32.1 x "	0.52

TABLE 15

Oct. 13, '20.

O-NITRO TOLUENE

Membrane Thickness	Solution Succinic	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
18-589	N/100000"	850.0	0	+	25°	5.5m.m.	0.600	70.5×10^{-5}	0.92
"	N/10000 "	"	0	+	"	5.5" "	0.568	66.8 x "	0.88
"	N/1000 "	"	0+	+	"	5.5" "	0.520	61.1 x "	0.89
"	N/100 "	"	0.5	+	"	4 " "	0.415	48.8 x "	0.87
"	Neutral NaOH	"	0	+	"	5 " "	0.654	76.9 x "	0.89
"	N/100000"	"	0	+	"	5 " "	0.732	86.1 x "	0.95
"	N/10000 "	"	0.5-	+	"	5 " "	0.754	88.7 x "	0.88
"	N/1000 "	"	1.0-	+	"	3.5" "	0.807	94.9 x "	0.92
"	N/100 "	"	1.0	+	"	7 " "	1.547	182.0 x "	0.90

EFFECT OF TEMPERATURE CHANGE

When runs were made on the pure solvent, under varying temperature conditions, keeping other factors constant, a smooth curve was produced which had the same general shape as the water curve and also as that obtained with other non aqueous solvents. Table 16 is for furfural, Table 17 for isopropyl alcohol, and Table 18 for o-nitrotoluene.

TABLE 16

Oct. 4, '20.

FURFURAL

Mem-brane Thick-ness	Solution Fur-fural	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
S-589	"	750.0	1.0	+	15.8°	4.5m.m.	0.185	24.6 x 10^{-5}	0.88
"	"	"	1.0	+	20.2°	3 " "	0.192	25.6 x "	1.08
"	"	"	1.0	+	25.0°	3 " "	0.202	26.9 x "	0.87
"	"	"	1.0	+	31.5°	5 " "	0.215	28.6 x "	1.00
"	"	"	1.0	+	40.0°	4 " "	0.227	30.2 x "	0.96

TABLE 17

Oct. 8, '20.

ISOPROPYL ALCOHOL

Mem-brane Thick-ness	Solution Isopro-pyl Al-cohol	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea-bility
S-589	cohol	859.0	1.0	+	16.8°	6 m.m.	0.544	63.3 x 10^{-5}	0.50
"	"	"	1.0	+	20.6°	5 " "	0.662	77.0 x "	0.55
"	"	"	1.0	+	25.0°	5 " "	0.717	83.4 x "	0.60
"	"	"	1.0	+	29.0°	4.5" "	0.752	87.5 x "	0.51
"	"	"	1.0	+	38.5°	5 " "	0.815	94.8 x "	0.56

TABLE 18

Oct. 18, '20.

O-NITRO TOLUENE

Mem-brane Thickness	Solution O-Nitro Toluene	Voltage	Current	Di-rection	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
:S-589	"	850.0	0	+	15.5°	4 m.m.	0.572	67.3 x 10^{-5}	0.89
"	"	"	0	+	21.2°	5.5" "	0.614	72.2 x "	0.85
"	"	"	0	+	25.0°	5 " "	0.654	76.9 x "	0.89
"	"	"	0	+	34.6°	5 " "	0.686	80.7 x "	0.90
"	"	"	0	+	42.3°	5 " "	0.711	83.6 x "	0.88

For Table 16.

Rate of Osmose

For Table 17.

Rate of Osmose

For Table 18.

Rate of Osmose
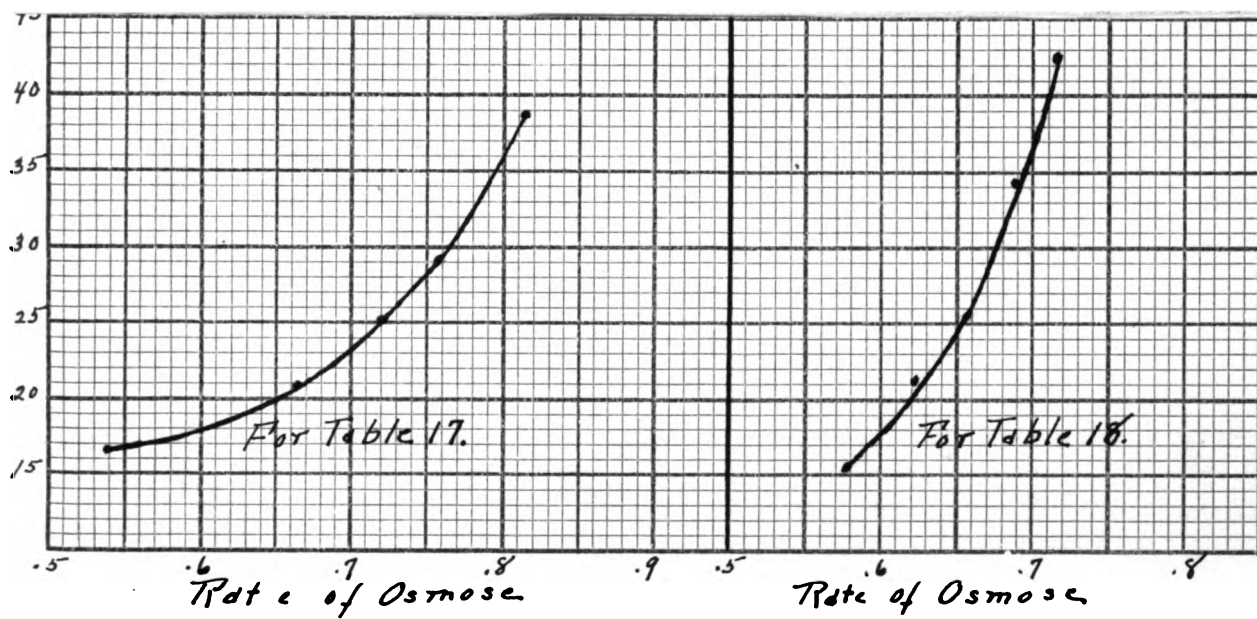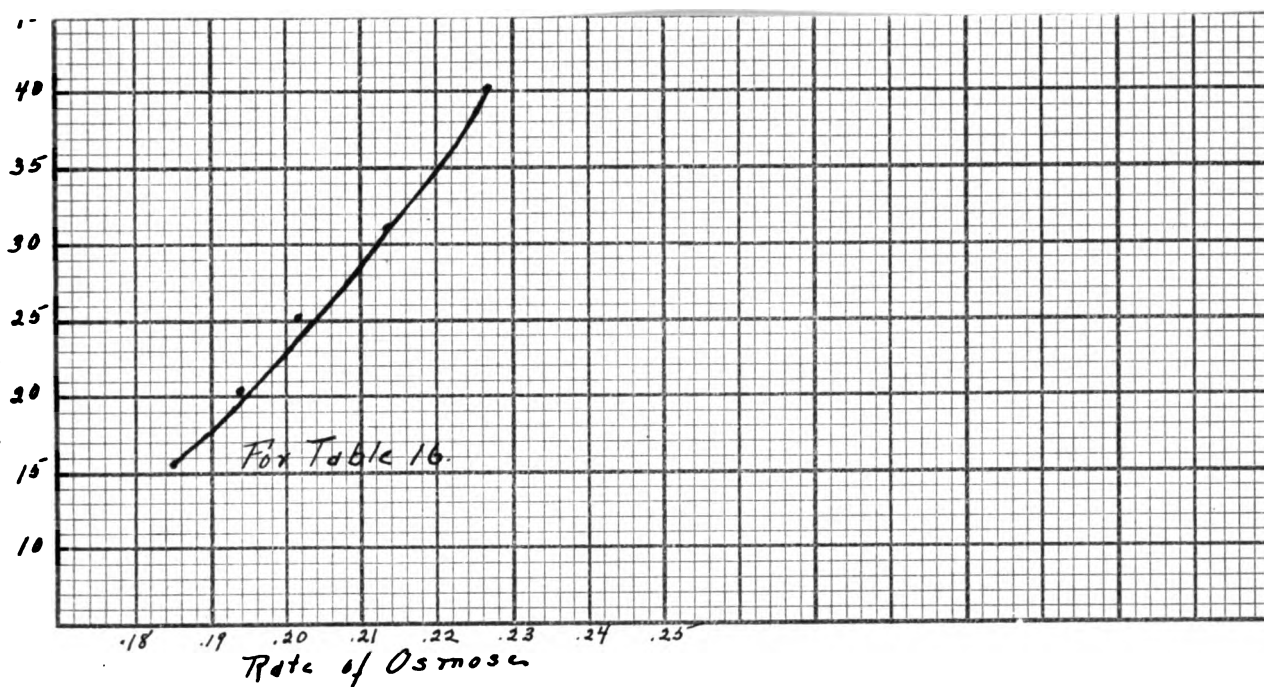
THE EFFECT OF THE ADDITION OF

CERTAIN SALTS

In order to keep this work uniform and to secure comparative results, the same set of salts was used. The original purpose of this series was to determine if any relationship existed between the valence of the ion and the rate of endosmose. No such rule as that promulgated by Perrin[1] or by Holmes[2] was found applicable. The results are found in the following tables: Table 19 shows the cation effect in furfural and Table 20 the anion effect. With isopropyl alcohol Table 21 for the cation and Table 22 for the anion are given. Table 23 gives the results of the cation effect in o-nitro toluene and Table 24 the anion effect in the same solvent.

1. Comptes Rendus. 136, 1388; 137, 513 (1903).
2. Doctors Dissertation - Johns' Hopkins University.

TABLE 19

Oct. 1, '20.

FURFURAL

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	"NaNO$_3$	750.0	8.0	-	25°	3.5m.m.	0.053	7.0 x 10^{-5}	0.92
"	"KNO$_3$	"	8.0	+	"	4.5" "	0.112	14.9 x "	1.03
"	"Ca(NO$_3$)$_2$	"	4.0	-	"	5 " "	0.528	70.4 x "	0.90
"	"Ba(NO$_3$)$_2$	"	1.5	+	"	5 " "	0.116	15.4 x "	0.96
"	"Al(NO$_3$)$_3$	"	3.5	-	"	3 " "	0.274	37.2 x "	1.05
"	"CrAc$_3$	"	1.5	+	"	5 " "	0.171	22.8 x "	0.93
"	"U Ac$_4$	"	2.0	+	"	4.5" "	0.031	4.1 x "	0.88
"	Pure Solvent	"	1.0	+	"	3 " "	0.202	26.9 x "	0.87

TABLE 20

Oct. 1, '20.

FURFURAL

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
bS-589	"KCNS	750.0	6.5	+	25°	4.5m.m.	0.118	15.7 x 10^{-5}	0.92
"	"CuAc$_2$	"	1.5	+	"	5.5" "	0.308	41.0 x "	1.03
"	"K$_2$SO$_4$	"	2.0	+	"	5 " "	0.325	43.3 x "	0.89
"	"K$_2$C$_2$O$_4$	"	3.0	+	"	4 " "	0.667	88.9 x "	0.85
"	"K$_3$PO$_4$	"	2.5	+	"	3 " "	0.510	68.0 x "	1.13
"	"Na$_3$Cit	"	2.0	+	"	6 " "	0.314	41.8 x "	0.98
"	"K$_4$Fe(CN)$_6$	"	1.5	+	"	4.5" "	0.298	39.7 x "	1.03
"	Pure Solvent	"	1.0	+	"	3 " "	0.202	26.9 x "	0.87

TABLE 21

Oct. 7, '20.

ISOPROPYL ALCOHOL

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	"NaNO$_3$	859.0	6.0	+	25°	5 m.m.	0.066	7.6 x 10^{-5}	0.53
"	"KNO$_3$	"	3.0	+	"	4 " "	0.259	30.1 x "	0.50
"	"Ca(NO$_3$)$_2$	"	4.0	-	"	4 " "	0.204	23.7 x "	0.54
"	"Ba(NO$_3$)$_2$	"	2.0	+	"	6 " "	0.309	35.9 x "	0.54
"	"Al(NO$_3$)$_3$	"	2.0	+	"	5.5" "	0.071	8.8 x "	0.56
"	"Cr Ac$_3$	"	2.0	+	"	6 " "	0.507	59.0 x "	0.50
"	"U Ac$_4$	"	1.5	+	"	5 " "	0.398	46.3 x "	0.54
"	Pure Solvent	"	1.0	+	"	5 " "	0.717	83.4 x "	0.60

TABLE 22

Oct. 8, '20.

ISOPROPYL ALCOHOL

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	"KCNS	859.0	6.0	+	25°	5.5m.m.	0.265	30.8×10^{-5}	0.53
"	"CuAC$_2$	"	2.0	+	"	6 " "	0.376	43.7 x "	0.50
"	"K$_2$SO$_4$	"	1.5	+	"	6.5" "	0.447	52.0 x "	0.55
"	"K$_2$C$_2$O$_4$	"	1.5	+	"	6 " "	0.545	63.4 x "	0.50
"	"K$_3$PO$_4$	"	1.5	+	"	5 " "	0.581	67.6 x "	0.50
"	"Na$_3$Cit	"	1.5	+	"	3 " "	0.533	62.0 x "	0.54
"	"K$_4$Fe(CN)$_6$	"	1.5	+	"	5 " "	0.554	64.4 x "	0.52
"	Pure Solvent	"	1.0	.+	"	5 " "	0.717	83.4 x "	0.60

TABLE 23

Oct. 15, '20.

β-NITRO TOLUENE

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	" NaNO$_3$	850.0	0	+	25^0	5.5m.m.	0.702	82.5 x 10^{-5}	0.92
"	" KNO$_3$	"	0	+	"	4 " "	1.572	185.0 x "	0.90
"	" Ca(NO$_3$)$_2$	"	0	+	"	3.5" "	0.808	95.0 x "	0.93
"	" Ba(NO$_3$)$_2$	"	0	+	"	3.5" "	0.738	86.8 x "	0.88
"	" Al(NO$_3$)$_3$	"	0.5	+	"	6 " "	2.415	284.1 x "	0.88
"	" Cr Ac$_3$	"	0	+	"	5 " "	0.796	93.4 x "	0.88
"	" U Ac$_4$	"	0	+	"	5 " "	0.811	95.4 x "	0.90
"	Pure Solvent	"	0	+	"	5 " "	0.654	76.9 x "	0.89

TABLE 23

Oct. 15, '20.

Q-NITRO TOLUENE

Mem-brane Thick-ness	Solution N/10000	Voltage	Current	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
48-589 "	" NaNO$_3$	850.0	0	+	25^0	5.5m.m.	0.702	82.5 x 10^{-5}	0.92
"	" KNO$_3$	"	0	+	"	4 " "	1.572	185.0 x "	0.90
"	" Ca(NO$_3$)$_2$	"	0	+	"	3.5" "	0.808	95.0 x "	0.93
"	" Ba(NO$_3$)$_2$	"	0	+	"	3.5" "	0.738	86.8 x "	0.88
"	" Al(NO$_3$)$_3$	"	0.5	+	"	6 " "	2.415	284.1 x "	0.88
"	" Cr Ac$_3$	"	0	+	"	5 " "	0.796	93.4 x "	0.88
"	" U Ac$_4$	"	0	+	"	5 " "	0.811	95.4 x "	0.90
"	Pure Solvent	"	0	+	"	5 " "	0.654	76.9 x "	0.89

TABLE 24

Oct. 15, '20.

O-NITRO TOLUENE

Mem-brane Thick-ness	Solution N/10000	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
S-589	" KCNS	850.0	1.0	+	25°	5 m.m.	3.254	382.3 x 10⁻⁵	0.88
"	" Cl Ac₂	"	0.5	+	"	3 " "	0.821	96.5 x "	0.89
"	" K₂SO₄	"	0.5	+	"	5.5" "	0.588	69.1 x "	0.85
"	" K₂C₂O₄	"	0	+	"	5 " "	0.536	63.0 x "	0.88
"	" K₃PO₄	"	0	+	"	3 " "	0.621	73.0 x "	0.90
"	" Na₃Cit	"	0	+	"	6 " "	0.488	57.2 x "	0.90
"	" K₄Fe(CN)₆	"	0.5	+	"	3 " "	0.570	67.0 x "	0.90
"	Pure Solvent	"	0	+	"	5 " "	0.654	76.9 x "	0.89

Let us note some of the specific peculiarities and irregularities in these runs which might be greatly multiplied by reference to Part I of this paper. Tables 19 (furfural) and 20 (isopropyl alcohol) show both the Na and K ions having a marked effect upon the rate of endosmose, the Na effect being much larger. In Table 23 (o-nitro toluene) these ions did not seem to be effective at all but the NO_3 ion was. $Ca(NO_3)_2$ supplying a bivalent cation, should show a greater effect than Na or K and it did in furfural and isopropyl alcohol, but not in o-nitro toluene. $Al(NO_3)_3$ should give an even greater effect. It did not do so in any instance and with o-nitro toluene it gave the maximum positive flow except for KCNS. In many cases, where in a water solution we have a highly adsorbed anion and only slightly adsorbed cation, the conditions are reversed in non aqueous solvents. There seems to be no other conclusion than that the adsorption for the different ions is a specific property of the solvent used and further, that the combination of ions in solution may also cause variations in such adsorption. This will be shown more strikingly in a later section under studies on the Hofmeister Series.

THE EFFECT OF VARYING THE CONCENTRATION
OF THE SALT IN SOLUTION

Just as in water, salts dissolved in non aqueous solvents manifest a maximum effect on the electric endosmose at a definite concentration. In the case of the solvents previously studied this concentration was about N/10000. With the three solvents under consideration this maximum effect seemed to come nearer N/1000. The most soluble salt was selected for each series. The results are shown in Table 25 and its curve for furfural, Table 26 for isopropyl alcohol, and Table 27 for o-nitro toluene.

TABLE 25

Oct. 4, '20.

FURFURAL

Membrane Thickness	Solution Ca(NO$_3$)$_2$	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	N/1000000 "	750.0	2.0	+	25°	4.5m.m.	0.206	27.6 x 10^{-5}	0.95
"	N/100000 "	"	2.0	+	"	5.5" "	0.189	25.2 x "	1.00
"	N/10000 "	"	3.0	-	"	3 " "	0.161	21.4 x "	0.90
"	N/1000 "	"	6.0	-	"	6 " "	0.387	51.6 x "	1.03
"	N/100 "	"	14.0	-	"	5 " "	0.183	24.4 x "	1.09

TABLE 26

Oct. 8, '20.

ISOPROPYL ALCOHOL

Membrane Thickness	Solution Ca(NO$_3$)$_2$	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	N/1000000 "	859.0	1.5	+	25°	3.5m.m.	0.593	69.0 x 10^{-5}	0.57
"	N/100000 "	"	2.0	+	"	5.5" "	0.478	55.6 x "	0.51
"	N/10000 "	"	2.5	-	"	7 " "	0.202	23.5 x "	0.54
"	N/1000 "	"	7.5	-	"	5 " "	0.284	33.0 x "	0.54
"	N/100 "	"	40.0	-	"	7 " "	0.183	21.3 x "	0.55

TABLE 27

Oct. 18, '20.

O-NITRO TOLUENE

Membrane Thick-ness	Solution Al(NO_3)$_3$	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	N/1000000 "	418.0	0	+	25°	6 m.m.	0.565	130.4 x 10^{-5}	0.88
"	N/100000 "	"	0	+	"	4 " "	0.606	142.5 x "	0.96
"	N/10000 "	"	0	+	"	5 " "	0.911	217.9 x "	0.85
"	N/1000 "	"	0	+	"	4 " "	1.228	293.7 x "	0.88
"	N/100 "	"	1.0	+	"	5 " "	0.713	170.5 x "	0.89

For Table 25.

To Cathode ←   → To Anode

$\frac{N}{100}$ $\frac{N}{1000}$ $\frac{N}{10000}$ $\frac{N}{100000}$ $\frac{N}{1000000}$

.2   .1   0   .1   .2   .3   .4

Rate of Osmose

For Table 26.

To Cathode ←   → To Anode

$\frac{N}{100}$ $\frac{N}{1000}$ $\frac{N}{10000}$ $\frac{N}{100000}$ $\frac{N}{1000000}$

.5   .4   .3   .2   .1   0   .1   .2

Rate of Osmose.

For Table 27.

$\frac{N}{100}$ $\frac{N}{1000}$ $\frac{N}{10000}$ $\frac{N}{100000}$ $\frac{N}{1000000}$

.6   .7   .8   .9   1.0   1.1   1.2   1.3

Rate of Osmose.
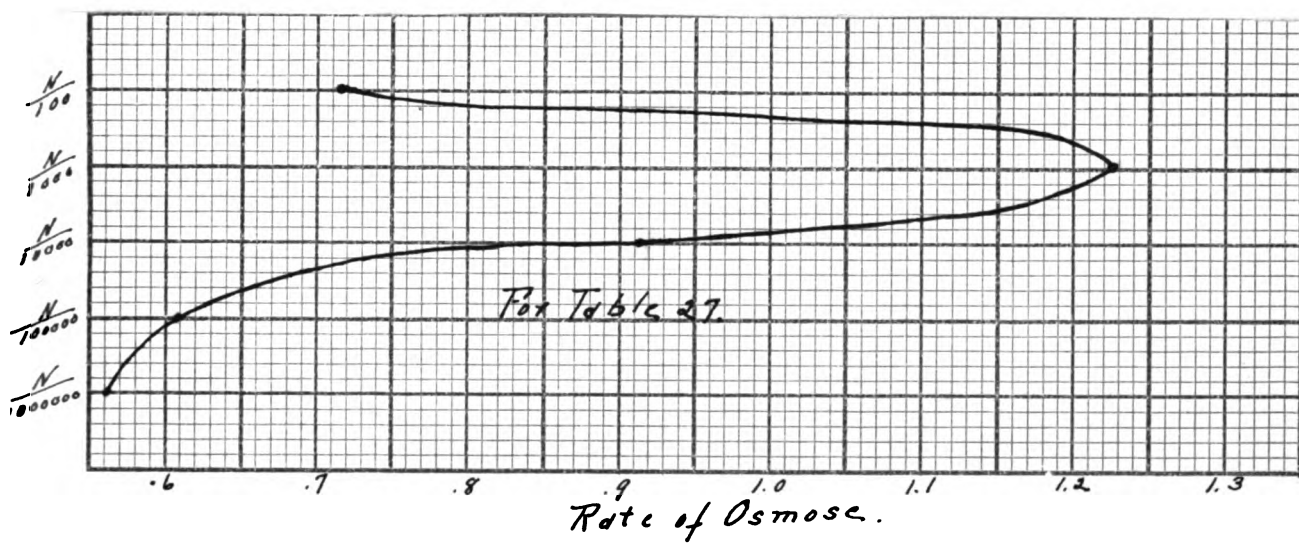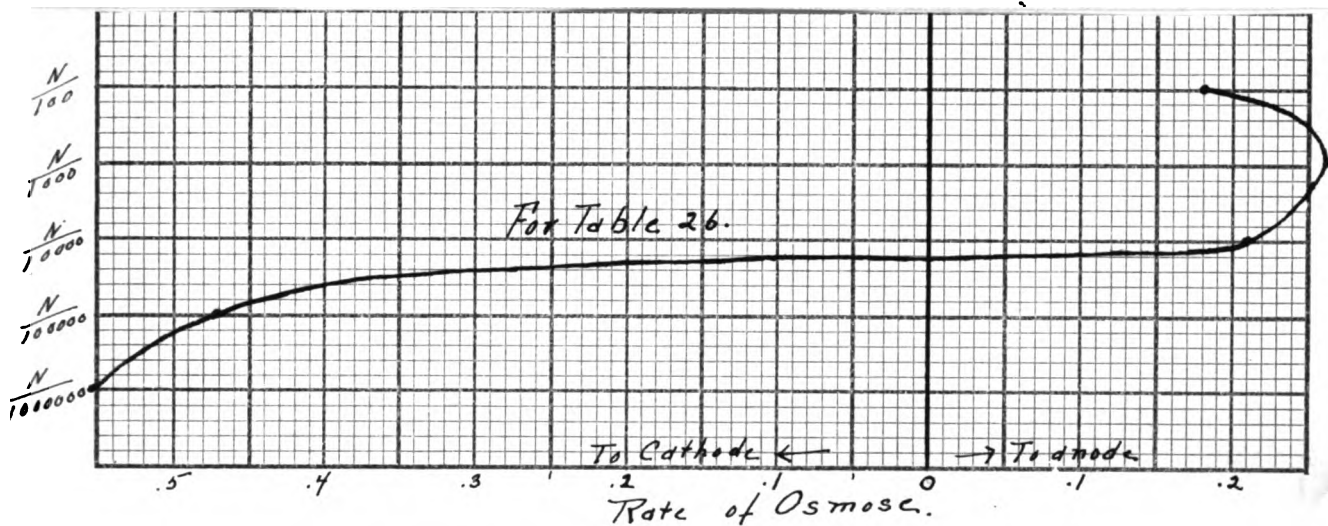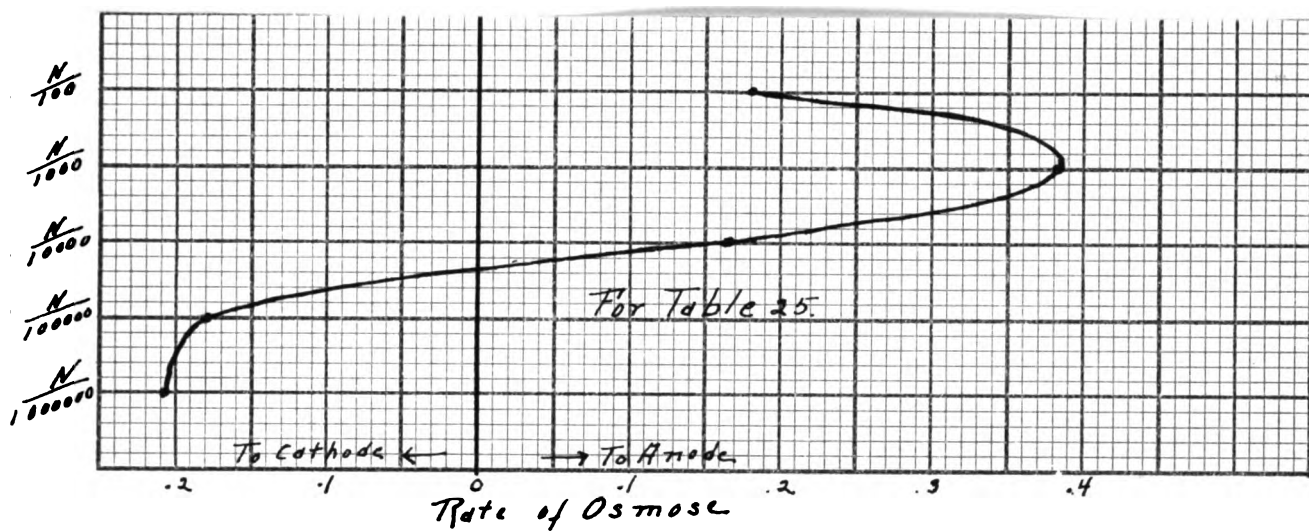
THE EFFECT OF ADDED WATER

Isopropyl alcohol was the only substance in this set sufficiently miscible with water to permit dilution runs. The curve for Table 28 shows the effect on the pure solvent and Table 29 the effect on the solvent containing a definite concentration of salt. These curves are interesting from the fact that they both contain a minimum. This same condition was observed with acetone containing $N/10000$ Na NO_3 but not with pure acetone. This may be partly due to chemical action between the alcohol and water and partly to the reversal of adsorption of the ions in water from that in the non aqueous solvent. A further explanation will be discussed from the standpoint of the "adsorption orientation" theory of electric endosmose.

TABLE 28   176

Oct. 11, '20.

ISOPROPYL ALCOHOL

Membrane Thickness	Solution % H_2O	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
kS-589	0	859.0	1.0	+	25°	5 m.m.	0.717	63.3×10^{-5}	0.50
"	1	"	1.5	+	"	7 " "	0.501	58.3 x "	0.53
"	5	"	2.0	+	"	5 " "	0.311	36.2 x "	0.55
"	10	"	2.0	+	"	6 " "	0.198	23.0 x "	0.57
"	25	"	2.5	+	"	4.5" "	0.136	15.8 x "	0.62
"	50	"	3.5	+	"	4 " "	0.126	14.6 x "	0.75
"	100	"	10.0	+	"	6 " "	0.529	61.5 x "	2.00

TABLE 29

Oct. 11, '20.

ISOPROPYL ALCOHOL + N/10000 KCNS

Membrane Thickness	Solution % H_2O	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
kS-589	0	859.0	6.0	+	25°	5.5 m.m.	0.265	30.8×10^{-5}	0.53
"	1	"	9.0	+	"	5.5" "	0.246	27.7 x "	0.51
"	5	"	9.0	+	"	6.5" "	0.173	20.1 x "	0.55
"	10	"	9.0	+	"	5.5" "	0.136	15.8 x "	0.54
"	25	"	9.0	+	"	5 " "	0.082	9.5 x "	0.58
"	50	"	14.0	+	"	5 " "	0.108	12.5 x "	0.61
"	100	840.0	24.0	+	"	6 " "	0.360	42.8 x "	1.76

For Table 28.

For Table 29.

Rate of Osmose.

Rate of Osmose.
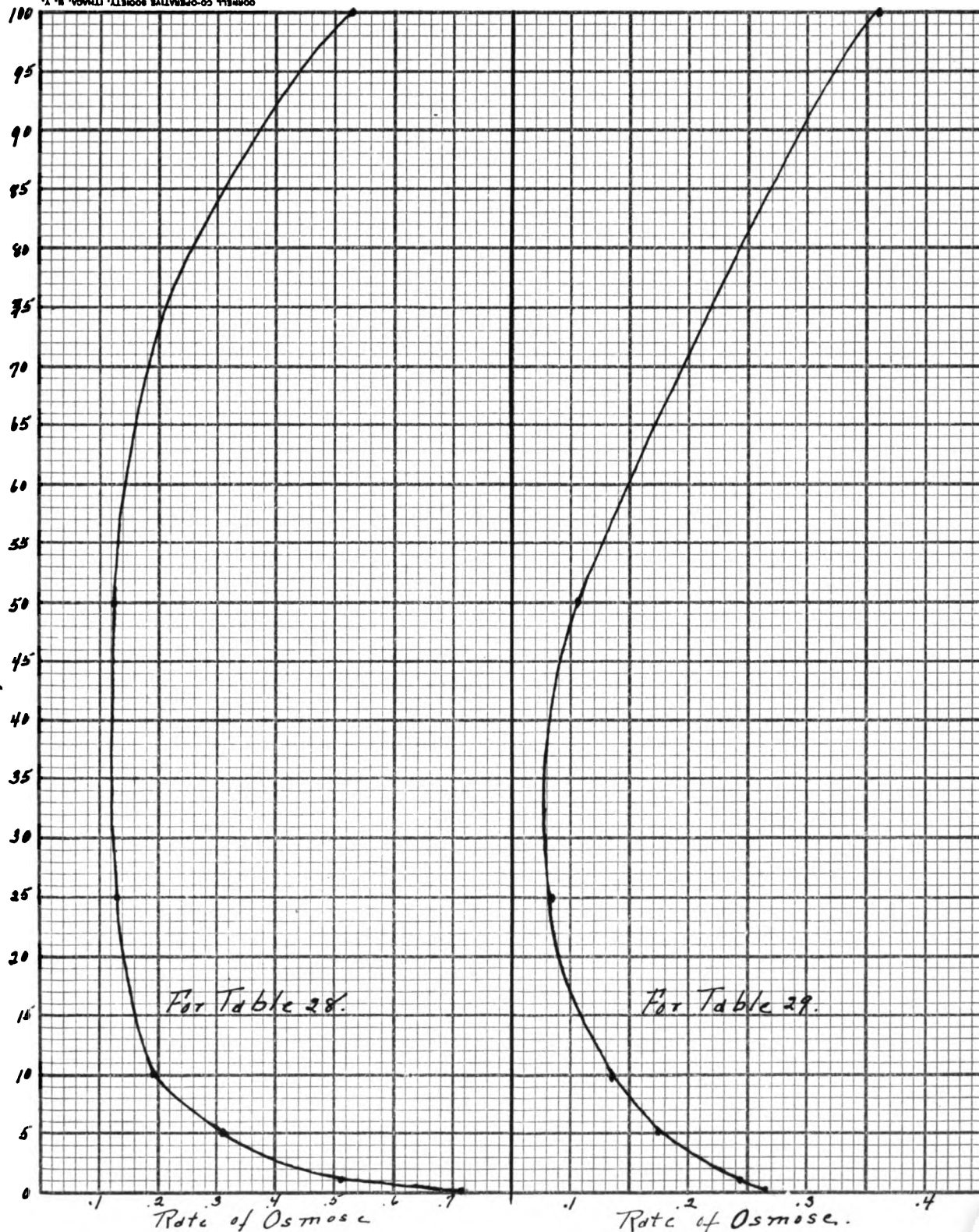
STUDIES ON THE HOF MEISTER SERIES

A study of the effect of certain salts dissolved in non aqueous solvents did not lead to any generalization comparable to that with water. The conclusion was drawn in Part I that, besides the factor of the selective adsorption of ions, there must be an additional specificity which is determined by the nature of the solvent used. It was found, for example, in the case of certain salts, that in one solvent the cation and in the other the anion would be most effective. Also, when considering a series, sometimes the order would be $Ca > Na$ or $Na > K$ and sometimes $Na > Ca$ or $K > Na$, etc. These examples were so numerous, as will be seen by studing the tables, that it could not be mere coincidence.

To throw more light on this question, it was decided to make a series of runs on various solvents using the salts ordinarily employed in the Hof meister Series. If electric endosmose is a purely adsorption phenomenon, as concluded by Briggs,[3] then it would seem that the order of anions and cations should be the same as the original series and further, it should be the same in each solvent. But, if other factors, such as the nature of the solvent and orientation, enter in, then the order would probably not be the same. Bethe and Toropoff[4] have carried out incomplete measurements in water which would indicate that the Hoffmeister order holds in this solvent. It was not possible to make a series

3. J. Physic Chem. 21, 198 (1919).

4. Zeit. Phys. Chemie, 89, 637 (1915).

of water runs with the battery system used, but the following solvents were studied: acetone, furfural, and n-butyl alcohol. The latter was selected because its normal endosmotic flow was negative.

The salts used for the anion series were: K_3Cit, $K_2Tartrate$, K_2SO_4, K Ac, K Cl, K NO_3, KClO_3, KI, KCNS, K_2CO_3, K Br and K_2HPO_4. Those for the cation series were: LiNO_3, NaNO_3, KNO_3 and Mg(NO_3)$_2$. N/10000 solutions were made up with the same precautions and technique as in previous work. The results are given in the following tables: Table 30 gives the effect of the anion in acetone and Table 31 the effect of the cation. With furfural, Table 32 shows the anion effect and Table 33 the cation effect. The results with o-nitro toluene are given in Table 34 for the anion and Table 35 for the cation.

TABLE 30

October 20, '20.

ACETONE

Membrane Thickness	Solution N/10000	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
S-589	" K_3Cit	364.0	0.5	+	25^0	6 m.m.	2.161	59.3 x 10^{-4}	4.76
"	" K_2Tartrate	"	0.5	+	"	5 " "	3.073	84.4 x "	4.54
"	" K_2SO_4	"	0.5	+	"	7.5" "	2.186	60.0 x "	5.00
"	" K Ac	"	1.5	+	"	3 " "	7.692	211.3 x "	4.76
"	" K Cl	"	0.5	+	"	3 " "	6.607	126.3 x "	4.34
"	" K NO_3	"	6.0	+	"	5 " "	0.474	13.0 x "	4.16
"	" K Cl O_3	"	6.0	+	"	5 " "	0.202	5.5 x "	4.54
"	" K I	"	10.0	+	"	3 " "	0.175	4.8 x "	3.84
"	"KCNS	"	12.0	−	"	6 " "	0.176	4.8 x "	4.00
"	" K_2CO_3	"	0.5	+	"	6 " "	3.597	98.8 x "	5.00
"	" K Br	"	5.0	+	"	4.5" "	2.276	62.5 x "	4.76
"	" K_2HPO_4	"	0.5	+	"	5 " "	3.086	84.7 x "	4.54

TABLE 31

Oct. 21, '20.

ACETONE

Mem-brane Thick-ness	Solution N/10000	Voltage	Cur-rent	Di-rec-tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permea bility
S-589	" LiNO$_3$	364.0	15.0	+	25°	3 m.m.	0.203	5.5 x 10^{-4}	4.16
"	" NaNO$_3$	"	6.0	+	"	6 " "	0.259	7.1 x "	4.34
"	" K NO$_3$	"	4.5	+	"	3 " "	0.414	11.3 x "	3.70
"	" NH$_4$NO$_3$	"	8.0	+	"	7 " "	0.106	2.9 x "	4.00
"	" Mg(NO$_3$)$_2$	"	3.0	-	"	4 " "	0.897	24.6 x "	4.16

TABLE 32

Oct. 22, '20.

FURFURAL

Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
Thickness	N/10000								
&S-589 "	K_3Cit	632.0	3.5	+	25^0	6 m.m.	0.340	5.3×10^{-4}	1.03
"	" $K_2C_4H_4O_6$	"	2.0	+	"	6.5" "	0.344	5.4 x "	1.06
"	" K_2SO_4	"	2.5	+	"	6.5" "	0.321	5.0 x "	0.95
"	" K Ac	"	3.0	+	"	5 " "	0.333	5.2 x "	0.93
"	" K Cl	"	4.0	+	"	7 " "	0.616	9.7 x "	1.00
"	" K NO_3	"	8.0	+	"	5 " "	0.092	1.4 x "	0.96
"	" K ClO_3	"	3.0	+	"	4.5" "	0.146	2.3 x "	0.88
"	" KI	"	7.0	+	"	7 " "	0.196	3.1 x "	1.11
"	" KCNS	"	11.0	+	"	5 " "	0.098	1.5 x "	1.08
"	" K_2CO_2	"	4.0	+	"	4.5" "	0.381	6.0 x "	1.00
"	" K Br	"	10.0	+	"	5 " "	0.330	5.2 x "	0.90
"	" K_2HPO_4	"	4.0	+	"	7 " "	0.311	4.9 x "	0.92

TABLE 33

Oct. 25, '20.

FURFURAL

n Mem. brane Thick- ness	Solution N/10000	Voltage	Cur- rent	Di- rec- tion	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permee- bility
S&S-589"	LiNO$_3$	632.0	12.0	-	25^0	3 m.m.	0.361	5.7 x 10^{-4}	0.96
"	" NaNO$_3$	"	6.0	-	"	5 " "	0.056	0.8 x "	0.89
"	" K NO$_3$	"	6.0	+	"	5.5" "	0.110	1.7 x "	1.01
"	" NH$_4$NO$_3$	"	8.5	+	"	4.5" "	0.062	0.9 x "	0.95
"	" Mg(NO$_3$)$_2$	"	6.0	-	"	3 " "	0.269	4.2 x "	1.00

TABLE 34

Oct. 27, '20.

N-BUTYL ALCOHOL

Membrane	Solution	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
Thickness	N/10000								
AS-589 "	K_3Cit	850.0	0.5	-	25°	5.5m.m.	0.302	3.5×10^{-4}	0.54
"	" $K_2C_4H_4O_6$	"	0.5	-	"	5 " "	0.207	2.4 x "	0.50
"	" K_2SO_4	"	0.5	-	"	6 " "	0.163	1.9 x "	0.53
"	" K Ac	"	1.0	-	"	6 " "	0.262	3.0 x "	0.54
"	" K Cl	"	1.0	-	"	5.5" "	0.487	5.0 x "	0.50
"	" K NO_3	"	1.5	-	"	3 " "	0.538	6.3 x "	0.50
"	" K Cl O_3	"	1.0	-	"	6.5" "	0.418	4.9 x "	0.50
"	" KI	"	2.0	-	"	6.0" "	0.535	6.2 x "	0.50
"	" KCNS	"	4.0	-	"	4.5" "	0.485	5.7 x "	0.57
"	" K_2CO_3	"	1.0	-	"	4.5" "	0.216	2.5 x "	0.50
"	" K Br	"	2.0	-	"	6 " "	0.564	6.6 x "	0.51
"	" K_2HPO_4	"	0.5	-	"	6.5" "	0.221	2.59x "	0.55

TABLE 35

Oct. 28, '20.

N-BUTYL ALCOHOL

Membrane Thick-ness	Solution N/10000	Voltage	Current	Di-rection	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
&S-589	" LiNO$_3$	850.0	4.0	-	25°	6.5m.m.	0.017	0.2 x 10^{-4}	0.56
"	" NaNO$_3$	"	2.0	-	"	5 " "	0.289	3.4 x "	0.50
"	" K NO$_3$	"	1.5	-	"	6.5" "	0.527	6.2 x "	0.57
"	" NH$_4$NO$_3$	"	3.0	-	"	5.5" "	0.115	1.3 x "	0.52
"	" Mg(NO$_3$)$_2$	"	1.5	-	"	5.5" "	0.210	2.4 x "	0.55

It will be noted that some of the endosmose rates are very nearly the same, as for example: K_3Cit and $K_2C_4H_4O_6$ in furfural, K Ac and K Br in furfural, K NO_3 and KCNS in furfural and KI and KNO_3 in n-butyl alcohol. A slight error in reading might reverse the order. Also, it must be assumed that the K ion, when considering the cation, must have the same effect in every case. It is doubtful if this is true but it is probably the particular combination of ions which is effective in producing the final results. For example: K combined with NO_3 may not have the same effect as K combined with Cl, the adsorption being modified by the presence of other ions. This feature will be studied at greater length in the near future.

Accepting, for the present, the assumption that the K ion effect is constant, the order of effect of the anions in acetone is:

Acetate > Cl > CO_3 > HPO_4 > Tartrate > Br > SO_4 > Citrate > NO_3 > ClO_3 > I > CNS

It will be noted in Table 30 that the endosmose with KCNS is negative. This would mean, when considering an original positive flow, that the CNS is the least effective ion of all, allowing enough adsorption of the K ion to reverse the flow. As for the others, those showing greatest flow would show greatest effect of the adsorbed anion. This rule would also hold in the case of furfural where the membrane in contact with the pure solvent also acquires a negative charge. The order of anion effect in furfural is as follows: (Table 32)

Cl > CO_3 > Tartrate > Citrate > Acetate > Br > SO_4 > HPO_4 > I > ClO_3 > CNS > NO_3 .

But when we consider n-butyl alcohol where the normal
flow is negative and hence, the membrane charge being positive, re-
verse conditions exist.   That ion which reduces the flow most is
most effective.   The order then becomes: (Table 34)
SO_4 > Tartrate > CO_3 > HPO_4 > Acetate > Citrate > ClO_3 > Cl > CNS > I > NO_3 > Br

There will be noted some very striking resemblances
in the various orders and also to the original Hoffmeister Series.
But there are also some very striking variations of order which can
only be explained by assuming a specific effect due to the nature
of the solvent.

This is even more marked when we consider the cations.
Assuming again, that the NO_3 ion is constant in effect, the order
of the cations in acetone is: (Table 31)

Mg > K > Na > Li > NH_4

From the "valence rule" we would expect Mg to come first, but this
order is entirely different from the accepted Hoffmeister Series
of the cations.

The order in furfural (Table 33) is:

Li > Mg > Na > NH_4 > K

and in n-butyl alcohol (Table 35):

K > Na > Mg > NH_4 > Li

These series eliminates both the valence rule, as also indicated
in the study on various salts, and the pure adsorption theory, which
would follow if the order were the same in every case.

DISCUSSION

In Part I of this paper it was suggested that the charge on the membrane might be considered as due to an orientation of the molecules of the solvent at the surface of contact of the membrane and liquid. It is purposed to consider this theory in greater detail.

In 1916 Langmuir[5] suggested that many of the conditions existing at the surface of a liquid, either in contact with its own vapor or with another liquid, might be accounted for by assuming an orientation of the molecules of the liquid at its surface. He continued this work in 1917[6] and reached some very definite conclusions regarding such orientation. His work was all on thin films. At this same time Harkins[7] and his co-workers were making an elaborate study of the "thermodynamic environment" of liquid surfaces and reached about the same conclusions. His work followed a paper by Frenkel[8] who had developed a mathematical theory of the surface electric double layer of solid and liquid bodies.

The work of Frenkel is extremely illuminating. Millikan[9] had shown that the existence of an electric double layer on the surface of metals was beyond a doubt. The only question was as to its origin. The old view that it was due to occluded gases,

5. Met. Chem. Eng. 15, 468 (1916).

6. J. Am. Chem. Soc. 39, 1848 (1917).

7. J. Am. Chem. Soc. 39, 354 (1917).

8. Phil. Mag. 33, 297 (1917)

9. Physics Rev. March, 1916.

chemical action, etc., had to be abandoned for a view which traced the potential to some intrinsic cause. Considering the atom to consist of a positive nucleus with electrons rotating about it, he has shown that these electrons constitute over the surface of the metal a layer of negative electrification with a corresponding layer of positive electrification on the inner side of the surface. This layer is atomic in thickness and prevents the escape of electrons. Similarly the double layers must exist on the surface of all liquids and amorphous solids, whatever their chemical composition. This being shown in a masterly mathematical thesis, he further considered surface tension forces as intimately related to contact electrification forces. Both are due to the same cause: an atomic or molecular electric double layer enveloping the surface of the solid and liquid bodies.

Harkins[10] then studied the total surface energy, free surface energy, latent heat and specific heat of the surface of a great many liquids and found some very striking regularities, when considering _different_ classes of substances. He concluded: "If we suppose the structure of the surface of a liquid to be at first the same as that of the interior, then the actual surface is always formed by the orientation of the least active portion of the molecule toward the vapor phase. If the molecule is monatonic and symmetrical, then the orientation will consist in a displacement of the electromagnetic fields of the atom. This molecular orientation sets up what is commonly called a 'double electric layer' at the surfaces of liquids and also of solids."

10. Loc. cit.

It should be noted here that this is the only time
Harkins alludes to this phenomenon as causing the charge on a
solid. All of his experimental work was with liquid surfaces.
It might also be added that this orientation will not necessari-
ly be the same when we have a liquid in contact with a solid,
as here the phenomenon is complicated by orientation in the
solid and adsorption.

Harkins found, if the rule was applied to special cases,
the following orientation was indicated: "In water the H atoms
turn toward the vapor phase and the O atoms toward the liquid.
With organic paraffine derivatives the CH_3 groups turn outward
and the most active group such as NO_2, CN, $COOH$, $COOM$, NH_2,
$NHCH_3$, COR, CHO, I, OH or groups which contain N, S, O, I or
double bonds turn toward the interior of the liquid." Now if
we bring another surface like water near the surface of this li-
quid the free energy of the water surface would decrease in a
manner depending primarily upon the most active or polar group in
the molecule and in a secondary way upon the shape of the molecule.
The solubility in water is related to this free energy decrease.
The active groups noted above, tend to go into the water surface
and pull into solution the slightly polar group, unless this other
group is too long or too large. This is also shown by the fact
that polar liquids are in general mutually soluble.

Further, "the equilibrium value of the interfacial free
energy between miscible liquids is always zero" but this must
change as the solubility decreases and be a maximum at the con-

tact of an insoluble membrane and liquid. This effect would be greatest in the case of electric endosmose where such conditions exist.

On the basis of the recent theory of the structure of the atom (a positively charged nucleus surrounded by widely separated negative electrons), it would seem plausible to expect stray fields of force and, as the electrons are in motion, these would be electromagnetic in nature. This would tend to cause orientation of the molecules throughout a liquid or solid. Now if a solid approaches a liquid in which it is soluble, or partially soluble; if a liquid approaches another liquid in which it is entirely or partially soluble; if a liquid is merely in contact with its vapor or finally, as in the case of electric endosmose, if we have a liquid in contact with an insoluble membrane, we might expect orientation to be an important factor in determining the "thermodynamic environment" at such contact. In the case of a large molecule, like many of our organic compounds, different parts of the same molecule might exhibit different solubilities. As in electric endosmose, there is obviously an adsorption factor, it might be added that different parts of the molecule might exhibit different adsorptions. If we have a very large or long molecule this might become quite apparent.

A liquid then, like a solid, might be considered as but a large molecule with a definite arrangement of atoms, according to Langmuir[11]. Alcohols all tend to arrange themselves so that the CH_3 groups are at the surface. If we consider this orientation phenomenon alone as determining the charge on a membrane brought in contact with the solvent, all the alcohols should establish

11. Loc. cit.

the same charge. But there is here an additional force of adsorption, strongly selective in nature. It asserts itself in the case of solvents, not merely by an adsorption of ions, but by adsorption of one end or one side of the larger molecules. As many organic substances are polar, this adsorption and orientation would establish a charge on the surface of the membrane. When a potential gradient is applied to the solution, bearing an opposite charge, it would tend to migrate through the membrane.

The nature of this charge can generally be predicted by Cohen's rule[12]. But in the case of alcohols and doubtless with other series of compounds, this is not always true. If we consider the OH group of the alcohol as being negative, then in the case of methyl, ethyl and isopropyl alcohols, the molecule is adsorbed with the OH group oriented toward the membrane. Further, these substances are completely soluble in water, hence the OH group would also tend toward a water layer. But n-butyl and amyl alcohols, which are not completely miscible with water, give negative endosmose. This would mean, either that the orientation is such that the positive end of the molecule is adsorbed or that the molecule is so large that there is only a small number of the OH groups to a large number of CH_3 groups. The OH effect might be reduced by pushing them farther apart, thus making the final effect apparently due to the adsorption of positive groups. Either supposition will explain the results so far as they have been studied. Hence, though the adsorption forces tend to arrange the molecule, as in the lower alcohols, it is too large and unwieldy and remains as in the surface of the solvent in contact with its vapor.

12. Wied. Ann. 64, 227 (1898).

Benzaldehyde gives positive endosmose, hence its negative group is oriented toward the membrane. With acetone the $C = O$ group is probably toward the membrane. So each solvent can be considered as presenting such an orientation picture. Isobutyl formate and iso amyl formate (Part I) may exhibit negative endosmose because the positive group is larger or more strongly adsorbed than the negative part of the molecule. It would seem, when using filter paper membranes, that most substances are oriented with the negative or most active (polar) group toward the membrane.

When salts are dissolved in the solvent, each ion, after being selectively adsorbed, produces its effect upon the established charge. This secondary effect is pure adsorption, if we eliminate the possibilities of chemical action. But the order of the effect is specific for the ion combination and for the solvent employed. This has been clearly shown in the experiments on the effects of certain salts and on the Hof meister Series. An ion effective in one solvent may be practically zero in effect in another solvent. Further, an increase in valence does not necessarily increase this effect, although chemical action might play an important role in the case of organic solvents, particularly under the influence of a high potential gradient.

The author has searched diligently for some marked change in the thermodynamic environment which would explain and account for these reversals, particularly in the alcohol series. No such variation was found but the study has led to the above theory as stated: a theory of adsorption orientation at the surface of contact of the liquid and membrane.

Considering Tables 1, 2 and 3 we see in the case of fur-
fural a rapid decrease in the rate of flow, showing the charge
quickly established on the membrane, the decrease being due
doubtless to chemical action and electrolysis. Isopropyl alcohol
and o-nitro toluene reach a maximum slowly, showing a slow orien-
tation of the molecule and a slow adsorption to attain the maximum
charge.

It does not seem necessary to add anything to the explana-
tion proposed for the change of endosmose rate with change of permea-
bility. (Part I). Duplication results require no explanation ex-
cept that changes in permeability rates may account for some of the
differences.

As the push or pull upon the liquid phase must be mea-
sured by the applied potential, an increase of voltage must
necessarily cause increased flow. This does not, however, appear
to be a linear function.

When we add to the solvent an acid or alkali, the ions
thus produced are bound to be selectively adsorbed by the membrane
and affect the originally established charge. This is pure adsorp-
tion and should reduce the flow with acid and increase with alkali,
unless in this particular solvent there is exhibited a specific
adsorption for the other ion. This, together with the possibility
of chemical action, will explain all the curves produced.

Increase of temperature decreases the viscosity of a
liquid and at the same time increases its mobility. This would
tend to increase the ease of orientation of the molecules and

their rate of adsorption, but not necessarily as a linear function.
Curves 16, 17 and 18 show this increase and have been previously
explained.

It does not seem necessary to add anything to the ex-
planation of the results obtained by the addition of various salts.
It has been shown to be a specific property of the solvent which
produces these effects. Adsorption and orientation are specific
as is also the effect of the solvent upon the selective adsorption
of certain ions.

Why the effect of a dissolved salt should be a maximum
at a definite concentration has been explained on the basis of
adsorption (Part I). This does not interfere with the theory of
orientation which applies only to the solvent molecules.

As water is added to a solvent it tends to orient
itself with the OH ion or O atoms at the surface of the membrane.
If the water molecules should be less highly adsorbed than those of
isopropyl alcohol, then the first additions of water would be merely
to dilute the surface layer charge by pushing the alcohol molecules
farther apart. As the per cent of water was increased the viscosity
would also decrease. Hence the endosmose would finally reach a
minimum, as shown by the curve, and then increase up to that of
100 per cent water. When a salt is dissolved in the solvent, the
problem is complicated by specificity of ion adsorption. The posi-
tive ion might be more highly adsorbed in the solvent and the re-
verse be true in water. This would tend to produce a smooth curve
without a minimum. If the reverse were true, the tendency would
be toward a maximum in the curve. It might even cause a reversal

through zero as shown in the pyridine curve and others in Part I.
The final curve must be a resultant of all of these factors tend-
ing to change the rate of endosmotic flow.

The studies on the Hoffmeister Series have been fully
discussed.

Some very peculiar results were noted when using certain
salts that require a word of comment. When NH_4NO_3 was dissolved in
furfural and readings taken, the bubble was almost stationary for
a period and then started toward the anode. As the flow continued,
it became slower and finally reversed toward the cathode. This
reversal took place at each reversal of current, the anode flow
becoming less and less each time and finally zero. The remaining
reversals of current gave only cathodic flow. The phenomenon was
repeated with KI in acetone, KCNS in isopropyl alcohol and in
several runs in the previous series. It was also noted in some
cases that the effect of the adsorbed ion was built up very slowly.
This latter might be due to a time element in adsorption. The
reversals, however, are probably due to an orientation of the
charge in the membrane pore due to different migration velocities
of the ions. Hence it is only apparent until adsorption is complete.
This assumption has formed the basis of most of the work of Bartell
and his co-workers[13] on free osmosis.

13. J. Am. Chem. Soc., 36, 646, (1914); 38, 1036; 1039 (1916)
    J. Physic.Chem. 24, 444 (1920).

SOME MATHEMATICAL CONCEPTIONS

The Smoluchowski equation for electric endosmose is given as

$$v = \frac{q \cdot e \cdot E \cdot D}{4\pi\eta\tau}$$

The only undetermined quantity here is e and this has been measured in the case of glass and water.[14] But this equation presents endosmose as a linear function of the applied potential, E. The curves obtained are, however, not linear and a correction seems necessary. A factor representing the permeability of the membrane does not appear at all, *in the above equation.* As the curves for this function are all of the same general shape an emperical factor might also be determined to represent this regularity.

Let us tabulate first (Table 36) the results as obtained for the various solvents used against a filter paper membrane. These are average results taken from duplication runs.

14. Cameron & Oettinger - Phil. Mag. 18, 586 (1909).

TABLE 36

olvent	Mem- brane	Volt- age	Cur- rent	Di- rec- tion	Temp.	cm/sec Osmose	cm/sec/volt Osmose	Dielectric Constant	Viscosity Coeffi- cient at Temp.
S&S-589 Thickness									
ter	8	289.0	5.8	+	25°	0.696	24.0×10^{-4}	80	0.00895 at 25°
etone	8	289.0	0	+	25°	0.510	17.6 "	20.7-33.8	0.00346 " 25°
yl lcohol	6	623.0	0	-	25°	0.158	2.5 "	10-30	0.04004 " 23°
tro- lenzene	8	555.0	0	-+	25°	0.725	13.0 "	34-42	0.01834 " 25°
ridine	6	841.0	0	+	26.5^o	0.083	9.8×10^{-5}	12.4	0.00877 " 25°
nzal- ehyde	8	954.0	0.5	+	25°	0.297	31.0 "	14-17	-------
Butyl lcohol	6	954.0	1.0	-	26°	0.188	19.7 "	18	0.02802 " 21.8^o
rfural	6	750.0	1.0	+	25°	0.202	26.9 "	41.7	-------
o propyl lcohol	4	859.0	1.0	+	25°	0.717	83.4 "	13.8	0.02221 " 22.2^o
Nitro oluene	6	850.0	0	+	25°	0.654	76.9 "	29.7	-------------

Viscosity data are taken from Landolt and Börnstein's Tabellen as are also the average dielectric constants. The membranes were constant in area being 32 m.m. in diameter. The length between the electrodes (l) was constant at 5.5 cm. As the calculations are carried out to cm/sec per volt, E is also a constant $= 1$

Hence $\dfrac{q\,E}{4\pi l}$ is constant $= 0.23$

and $v = 0.23 \times \dfrac{e\,D}{\eta}$

e is unknown but v can be obtained by multiplying the rate of osmose by a factor 0.125 which represents the average volume in c.c. of one cm. of the bubble tube.

Making no corrections for temperature or permeability variations we obtain (substituting in the above) for:

Water $0.125 \times 24.0 \times 10^{-4} = e_1 \times 0.23 \times 8938.5$

Acetone $0.125 \times 17.6 \times 10^{-4} = e_2 \times 0.23 \times 7861.2$

Amyl Alcohol $0.125 \times 2.5 \times 10^{-4} = e_3 \times 0.23 \times 499.5$

Nitro-Benzene $0.125 \times 13.0 \times 10^{-4} = e_4 \times 0.23 \times 2071.9$

Pyri-dine $0.125 \times 9.8 \times 10^{-5} = e_5 \times 0.23 \times 1413.9$

N-Butyl Alcohol $0.125 \times 19.7 \times 10^{-5} = e_6 \times 0.23 \times 642.3$

Isopro-pyl Alcohol $0.125 \times 83.4 \times 10^{-5} = e_6 \times 0.23 \times 621.3$

These equations if used in calculating e would give values of an order of magnitude much smaller than those of Cameron and Oettinger.[15] But here the voltage is considered a

15. Loc. cit.

linear function and permeability has not been taken into account.

Let us consider the correction necessary to apply to the equation as derived from the voltage against rate of endosmose curves. Both the linear function and the curve obtained must pass through the origin as when voltage is zero the endosmose must be zero. The curves obtained experimentally in both parts of this paper were plotted on logarithmic paper as shown in the accompanying chart. It will be noted that each curve approximates a straight line within the range of experimental error. The error here is probably large when we consider that the capillary bubble tube is bound to exhibit more frictional resistance when the solvent is moving slowly than when moving rapidly. This factor would tend to assist in shaping the curve.

The equation for such curves would be

$$v = K \times E^m$$

where m is the slope of the curve and K the intercept on the horizontal axis. It should be noted that these curves are drawn with the variable v on the horizontal axis and as slopes are ordinarily measured the equation should read $v = K \ E^{\frac{1}{b}}$. Here m is considered as equal to $1/b$ and is therefore measured by dividing the horizontal by the vertical components. The curves are so drawn to compare with those on plain graphing paper.
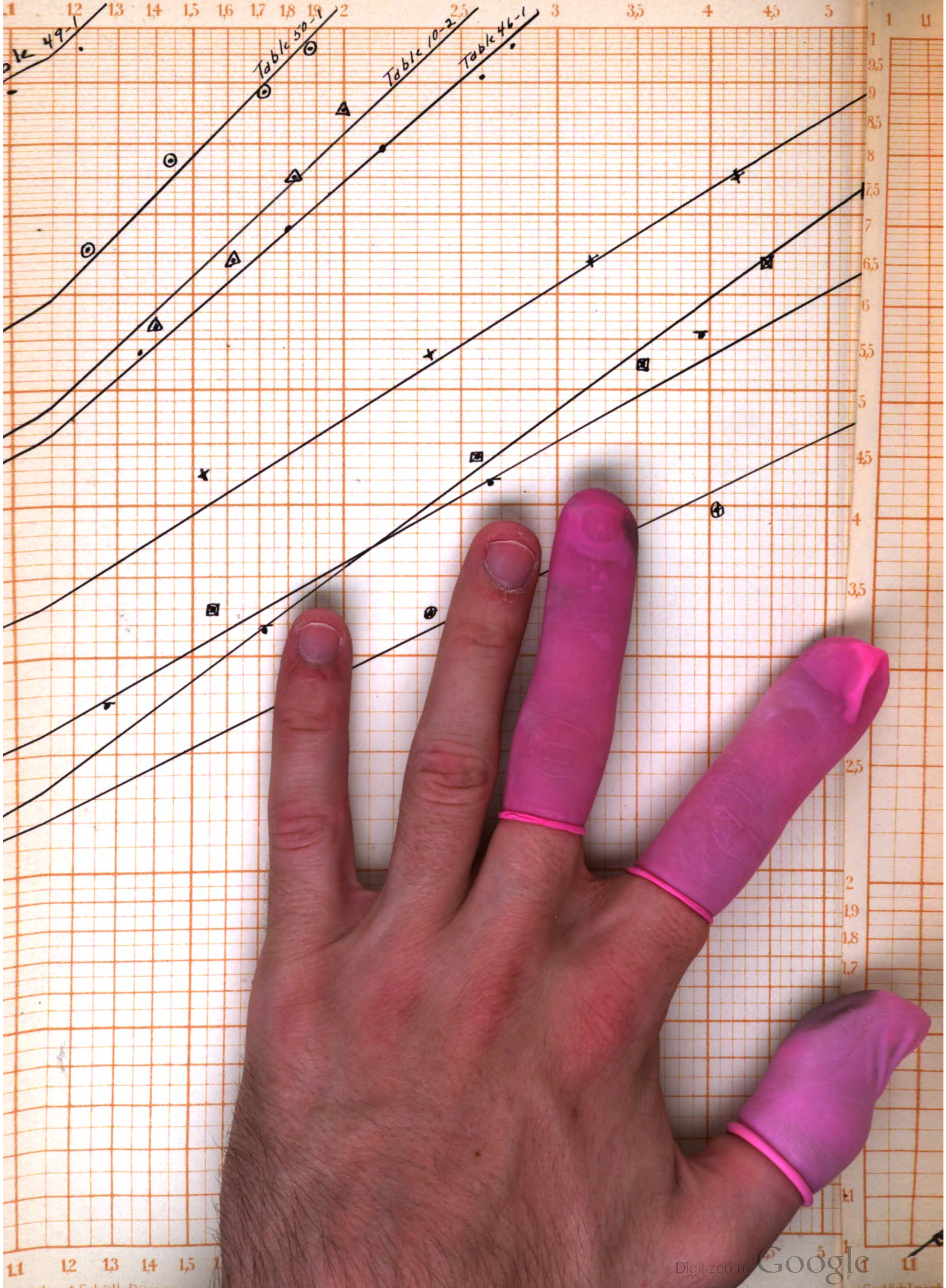
If $m = 1$ then the curve becomes a straight line on ordinary plotting paper. But in these curves the slope is generally greater than 1. This relationship applied to the general equation would give
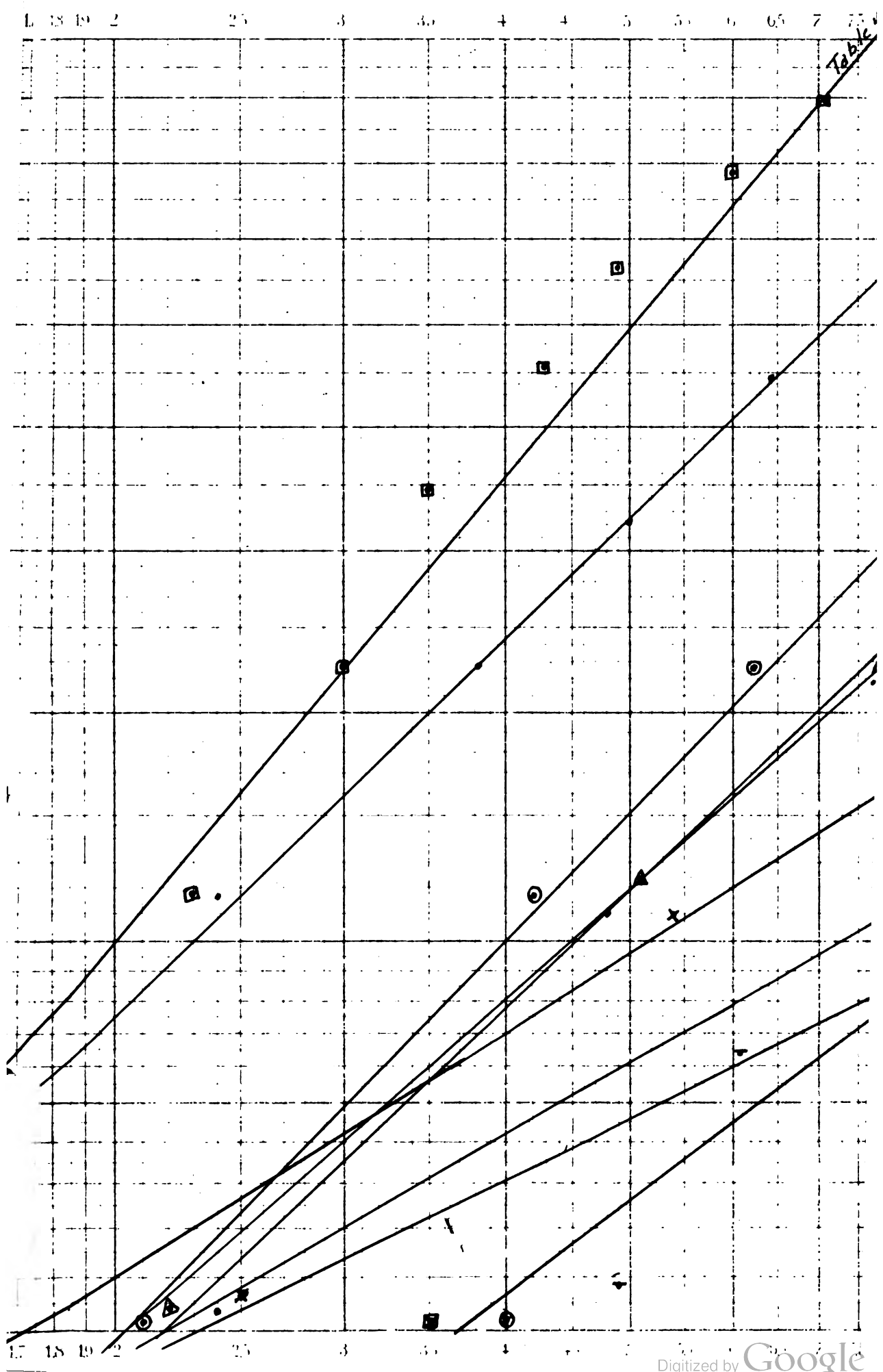
$$v = \frac{(K \ E^m) \ q \ e \ D}{4 \ \pi \ \eta \ l}$$

where K and m are constants depending upon the solvent and deter-

Table 49-1

Table 50-1

Table 10-2.5

Table 46-1

Schleicher & Schüll, Düren.

Carl Schleich

Table
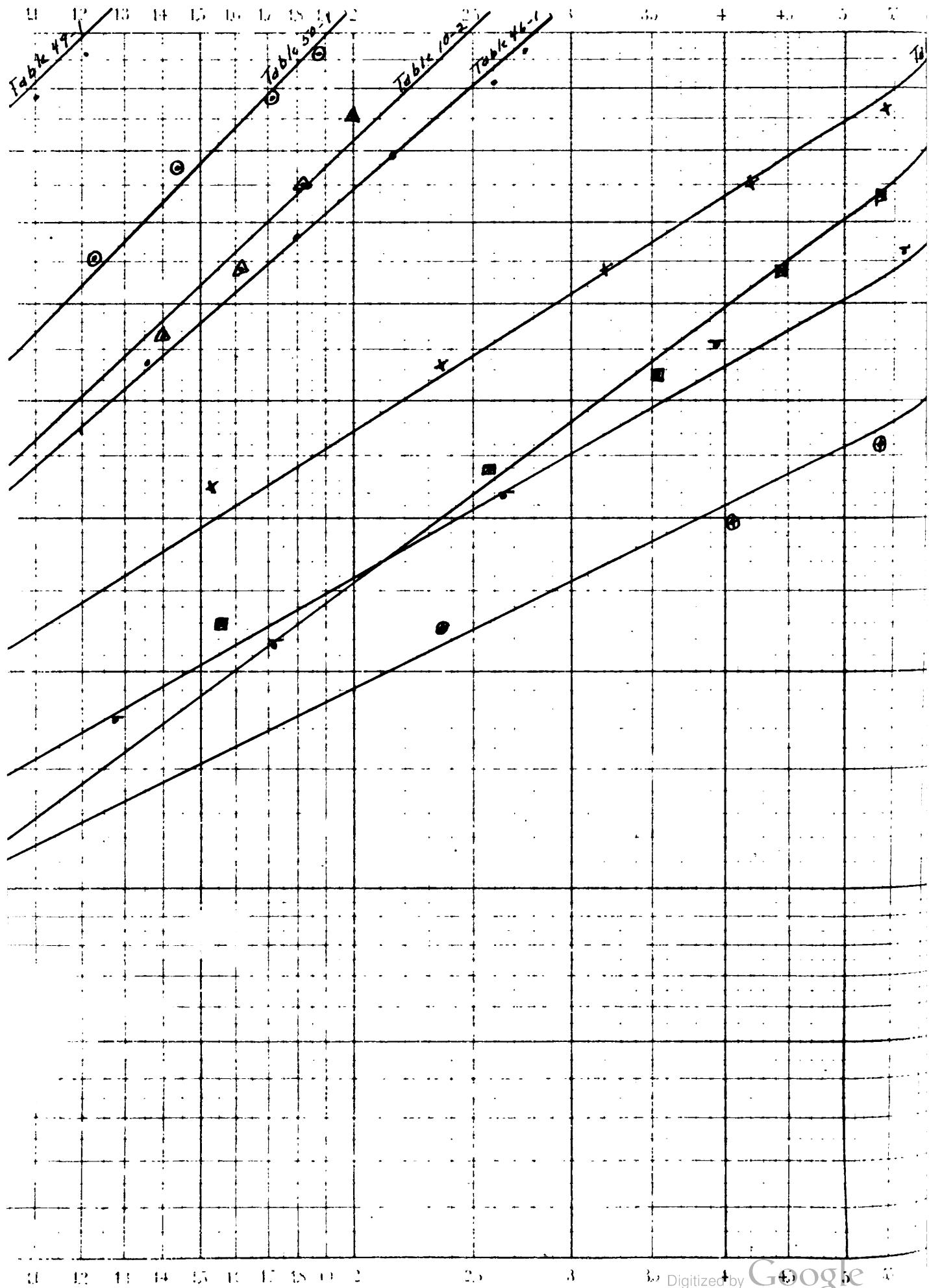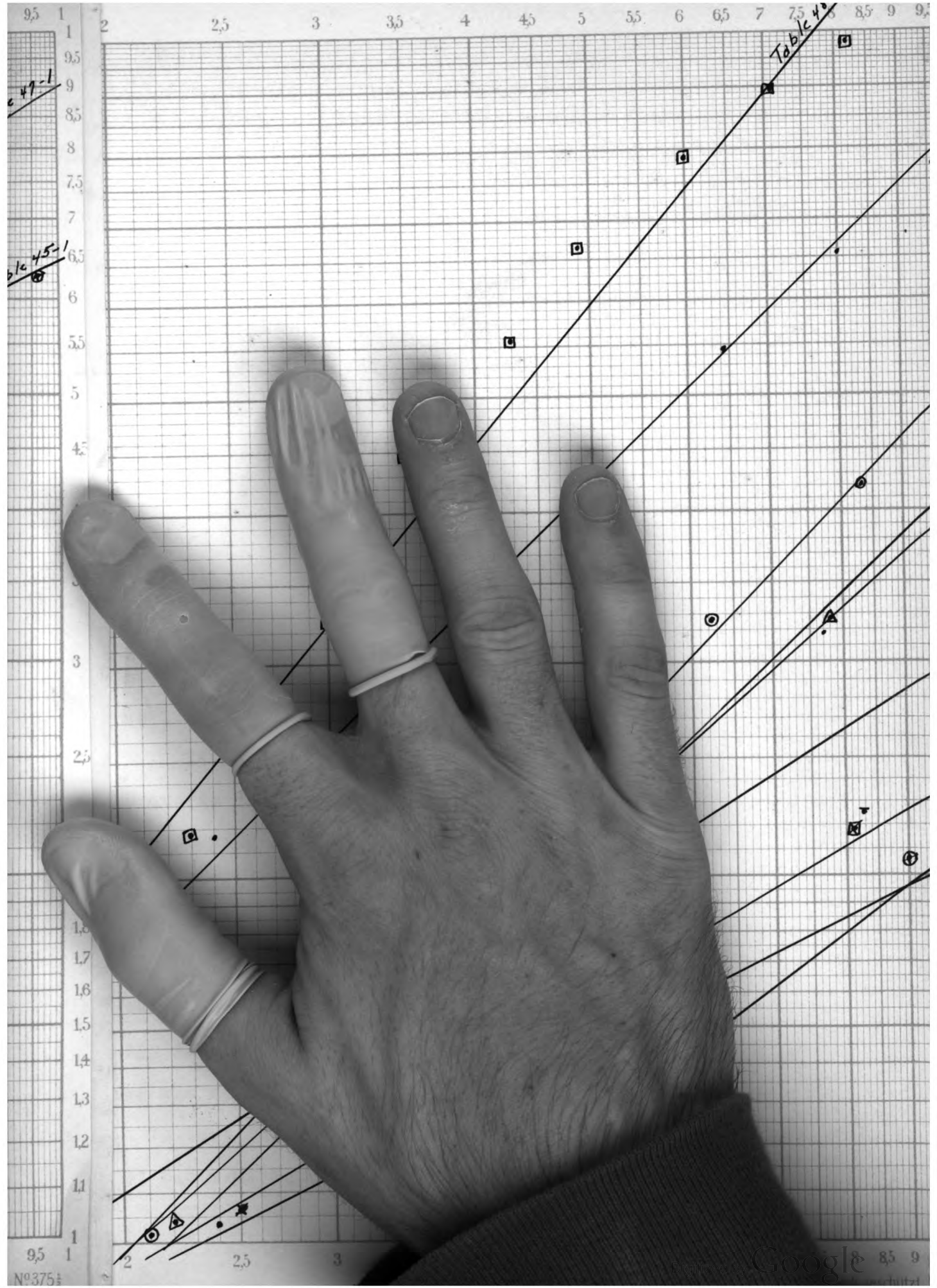
mined by the slope of the logarithmic curve. These values were carefully measured in several cases and gave the following results for m and K

	m	K
Furfural	1.06	0.0220
Isopropyl Alcohol	1.63	0.0168
O-Nitro toluene	1.47	0.0370
N-Butyl Alcohol	1.01	0.0202
Benzaldehyde	1.04	0.0112
Pyridine	0.90	0.0112
Nitrobenzene	1.75	0.0220
Amyl Alcohol	1.16	0.0205
Water	2.12	0.0228

The introduction of these values would not affect the remaining runs as the voltage was kept constant.

It has been suggested that this correction might be partly due to friction in the capillary bubble tube. If this were the shaping factor, then the curve of a substance like acetone, where the friction is almost negligible, should be more nearly linear than for the alcohols used. It is not. In fact, the more viscous substances varied least from a straight line, though this was partly due to a piling up in the electrode chambers when applying high voltages. These more viscous liquids passed through the membrane faster than they could pass through the bubble tube. To test this, the apparatus was set up with a measuring tube of 5.5 m.m. internal diameter. The movement was so slow with

isopropyl alcohol that the tube was changed for one 4.3 m.m.
in diameter. The results in Table 37 were obtained. By this
time some of the batteries were entirely useless so that high
voltages were not attainable but the curve is no nearer a
linear function than before exeept for its central portion.
There might still be a slight capillarity at the stop cook, but
it does not seem plausible as causing the regular variation
noted in the mathematical derivation of such curves. This
phenomenon is being studied further.

TABLE 37

Dec. 1, '20.

ISOPROPYL ALCOHOL

Membrane Thickness	Solution Isopropyl Alcohol	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose
48-589	"	697.0	0	+	25°	8 m.m.	0.178	25.5×10^{-5}
"	"	628.0	0	+	"	"	0.112	17.8 x "
"	"	525.0	0	+	"	"	0.084	14.0 x "
"	"	418.0	0	+	"	"	0.060	14.3 x "
"	"	365.0	0	+	"	"	0.052	14.2 x "
"	"	312.0	0	+	"	"	0.048	13.2 x "
"	"	259.0	0	+	"	"	0.024	9.2 x "
"	"	155.0	0	+	"	"	0.017	10.9 x "
"	"	104.0	0	+	"	"	0.012	11.5 x "

For Table 37.
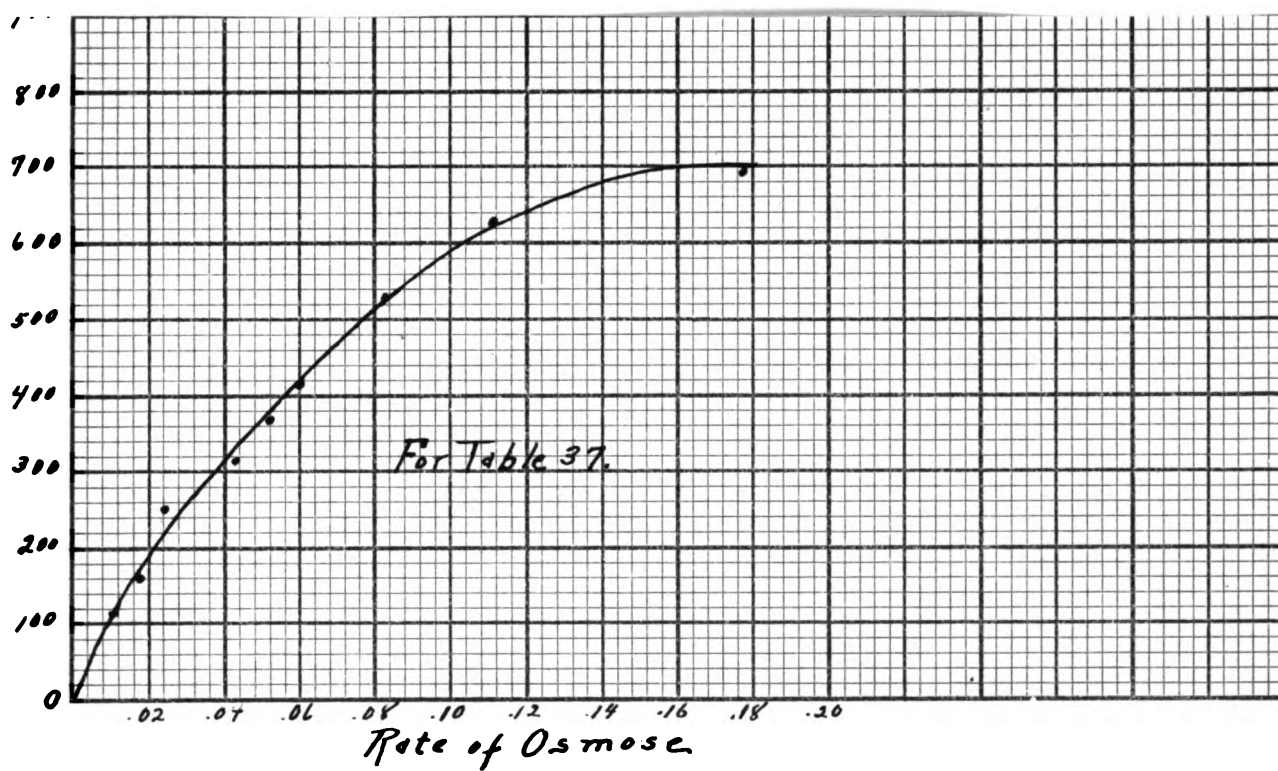
Rate of Osmose

Now let us observe the curves for rate of permeability against rate of endosmose. The portion of these curves below the maximum approximates in every case a straight line through the origin and the point of maximum endosmotic flow. This must be true, because as the membrane is increased in thickness and the permeability rate approaches zero, the endosmotic rate must also approach zero as a limit. The equation for such a curve would be:

$$v = K_1 \, p \qquad (1)$$

where v is the endosmose rate as before and p the rate of permeability as measured experimentally.

The upper portion of these curves is not so simple. These curves were also plotted on logarithmic paper (accompanying chart) and found to approximate straight lines. This would give as a relationship representing the upper portion of the curve:

$$v = K_2 \, p^{-a} \qquad (2)$$

where (p) is the rate of permeability, (a) the slope of the curve and (K_2) its itercept on the horizontal axis. Here again the slope must be determined by dividing the x or horizontal component by the y or vertical component. This relationship of $v = K_2 \, p^{-a}$ holds up to a thickness of membrane giving maximum rate of endosmose. Beyond this point the rate of endosmose is a linear function of the rate of permeability represented by p. This maximum cannot be predicted, as it varies with both solvent and membrane, and must be determined experimentally.

The porosity of the membrane is inversely proportional to the rate of permeability.
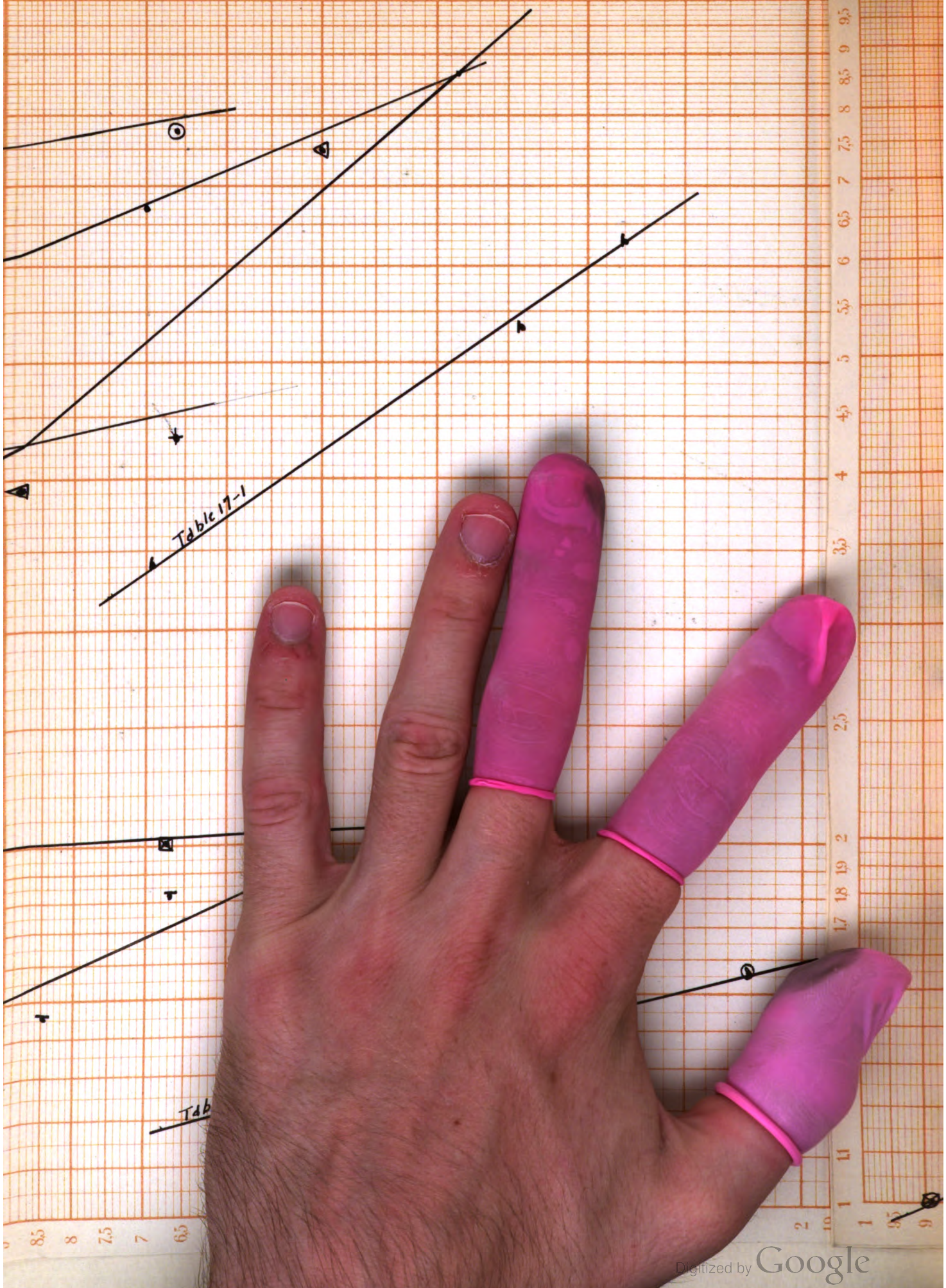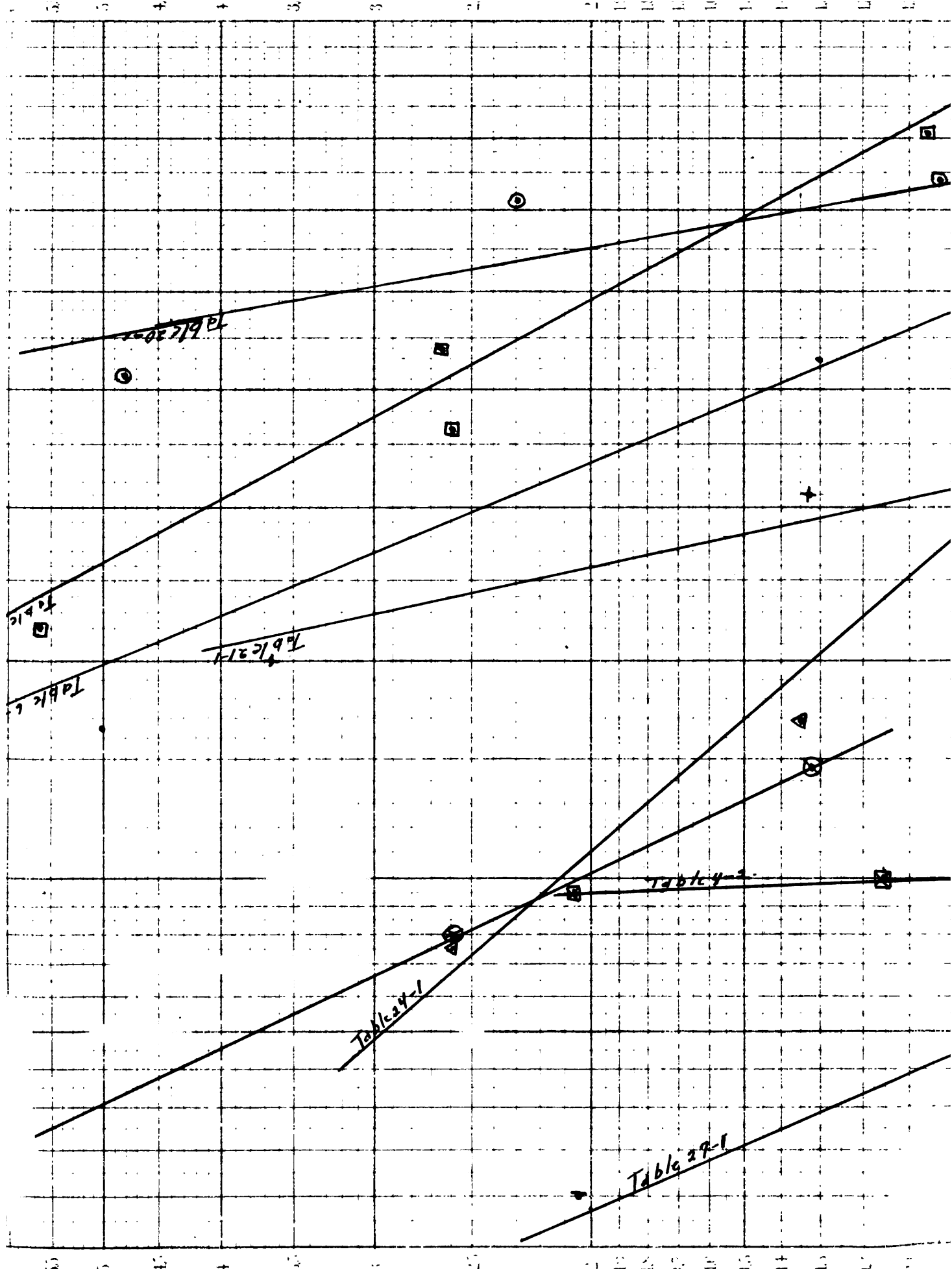
Table 19-1

Table 23-1
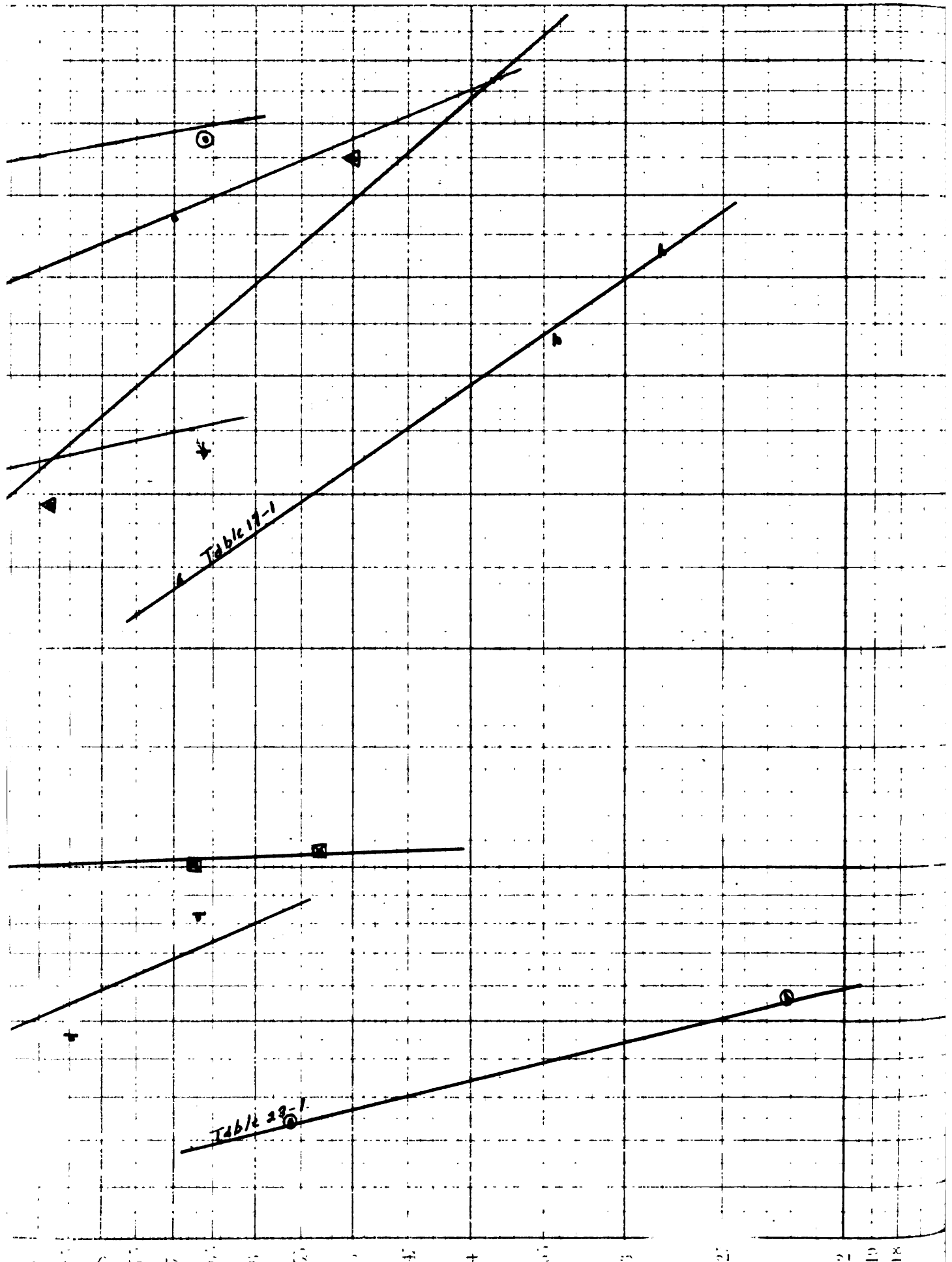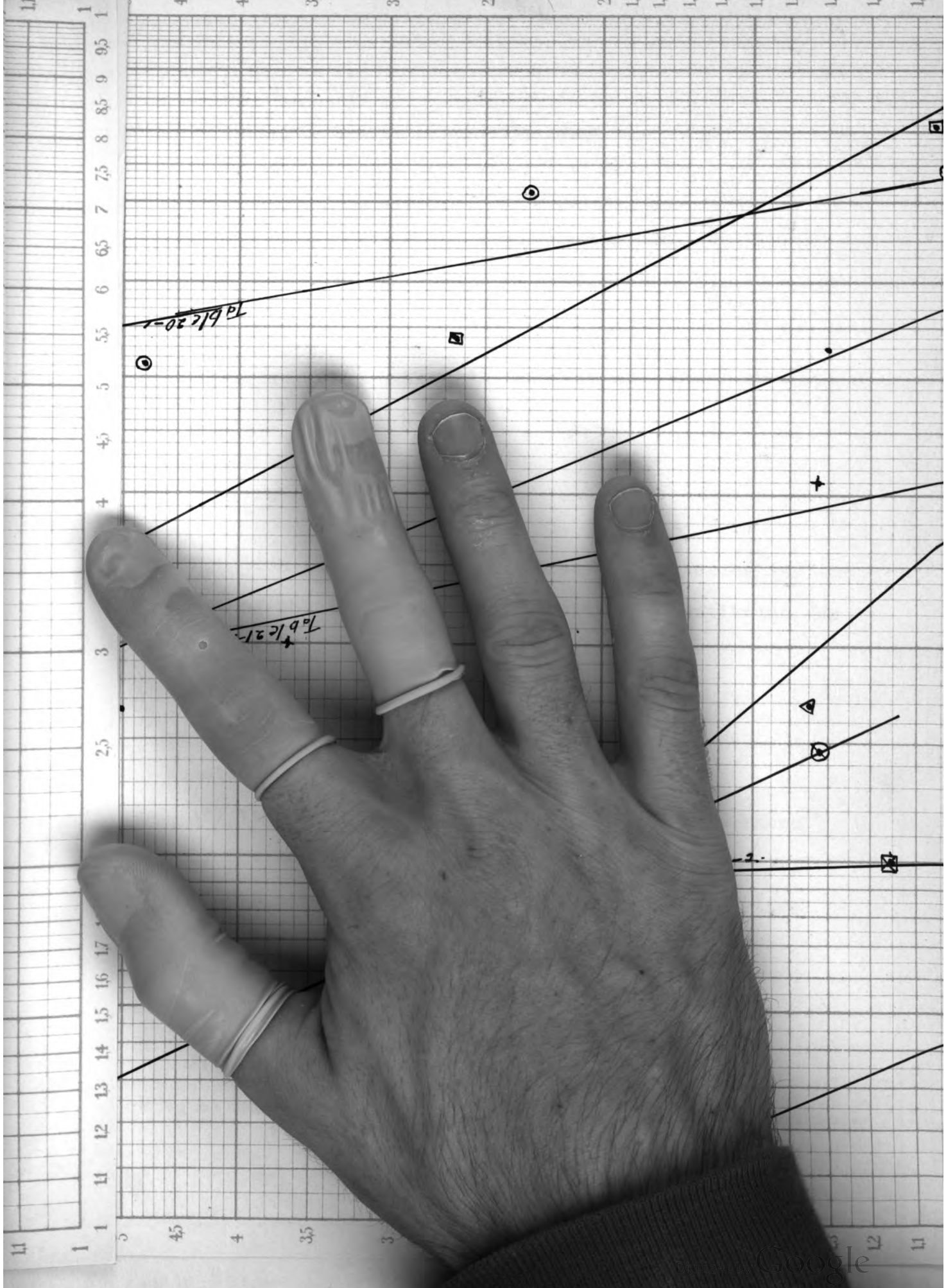
Table 17-1

If P represents the porosity then

$$p = \text{constant} \times \frac{1}{P} = \frac{h}{P}$$

substituting in equation (1)

$$v = K_1 \frac{h}{P} = (K_1 \, h) \; P^{-1}$$

representing this new constant by H_1

$$v = H_1 \, P^{-1} \qquad (3)$$

substituting in equation (2)

$$v = K_2 \, (\frac{h}{P})^{-2} = (K_2 \, h^{-2}) \; P^2$$

or representing this new constant by H_2

$$v = H_2 \, P^2 \qquad (4)$$

Equation (3) represents the lower and equation (4) the upper portion of the curve when the porosity is substituted for rate of permeability.

From (3) $P = H_1/v$

From (4) $P = \sqrt[2]{v}/H_2$

and the equation becomes $(P - H_1/v) \, (P - \sqrt[2]{v}/H_2) = 0$.

All the factors in equations (1) and (2) are known leaving only the undetermined (h). But as the same grade of filter paper was used in every case we may, for all practical purposes, take $p = 1/P$.

Substituting as above, we get

From (1) $P = K_1/v$

From (2) $P = \sqrt[2]{v}/K_2$

and the equation $(P - K_1/v) \, (P - \sqrt[2]{v}/K_2) = 0$ containing measurable quantities.

It was thought advisable to study one solvent through a wider range of porosity variations. Accordingly, isopropyl alcohol was selected and the results are shown in Table 58 and its accompanying curve. This fixes the contention that the maximum is sharp and definite, and that the curve for decreasing rate appears to be a straight line through the origin.

TABLE 38

Dec. 3, '20.

Isopropyl alcohol vs S&S Paper, No. 589.

Membrane Thickness	Solution Isopropyl Alcohol	Voltage	Current	Direction	Temp.	Bubble	cm/sec Osmose	cm/sec/volt Osmose	cm/sec Permeability
1	"	575.0	0.5	+	25°	5 m.m.	0.152	26.4 x 10^{-5}	1.50
2	"	"	"	+	"	5.5" "	0.176	30.6 x "	0.83
3	"	"	"	+	"	4 " "	0.220	38.2 x "	0.62
4	"	"	"	+	"	6 " "	0.284	49.5 x "	0.50
5	"	"	"	+	"	5.5" "	0.310	53.8 x "	0.46
6	"	"	"	+	"	4.5" "	0.274	47.6 x "	0.42
7	"	"	"	+	"	4 " "	0.218	37.6 x "	0.30
8	"	"	"	+	"	3 " "	0.197	34.2 x "	0.27
9	"	"	"	+	"	4 " "	0.165	28.6 x "	0.20
10	"	"	"	+	"	6.5" "	0.147	25.5 x "	0.18
11	"	"	"	+	"	6 " "	0.133	23.1 x "	0.17
12	"	"	"	+	"	5 " "	0.120	20.8 x "	0.17